

White Paper Report

Report ID: 105403

Application Number: PR-50141-12

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Institution: University of Wisconsin, Madison

Reporting Period: 1/1/2012-8/31/2015

Report Due: 11/30/2015

Date Submitted: 12/18/2015

NEH White Paper (December 2015)

Project Title: Investigation of Cellulose Nitrate Motion Picture Film Chemical Decomposition and Associated Fire Risk

Project ID Number: PR-50141-12

Home Institution: University of Wisconsin-Madison

Project Partners: Wisconsin Center for Film and Theater Research (UW-Madison), Wisconsin Historical Society, and UW-Madison Department of Chemistry

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DISCLAIMER: This white paper details findings from a research study commissioned by the National Endowment for the Humanities. No part of this paper shall be construed as recommendations for the storage and handling of nitrate film. The project participants and preparers of this paper are in no way liable for any incidents stemming from nitrate film storage handling procedures derived from the limited and preliminary research findings presented herein.

Investigation of Cellulose Nitrate Motion Picture Film Chemical Decomposition and Associated Fire Risk – A White Paper

Executive Summary

Goal

The purpose of the Wisconsin Nitrate Film Project was to understand the chemical processes by which nitrate decomposes and to ascertain whether deteriorated nitrate film stock is more dangerous than nitrate stock in good condition.

Methods

Donated film samples were analyzed visually and subjected to a battery of chemical and physical analyses. One roll in nearly pristine condition was selected for further testing in a 360-day, 60 °C accelerated aging protocol (corresponding to 55.7 years of storage in a 36 °F refrigerator or 220 years in a 0 °F freezer) that incorporated three relative humidity conditions (30 %RH, 50 %RH and 80 %RH) intended to mimic a variety of archival storage conditions. Additionally, brown powder samples donated to the project were tested for shock- and friction-sensitivity. Our research utilized a sample set of seven rolls of motion picture film and four collections of brown powder. Although this sample set may appear limited, it is of comparable magnitude to those used in previous investigations of nitrate decomposition.

Major Hypotheses

- A correlation exists between the chemical behavior of the film as quantified through rigorous analysis, and what we can see and measure on the film stock with the naked eye and simple tools.
- Combustibility of nitrate films increases in the later stages of decomposition.
- Brown powder is neither shock- nor friction-sensitive.

Results in Brief

Our studies up this point indicate that the five-stage classification model accurately correlates with only a few physical, chemical, and flammability properties of cellulose nitrate films. Alternative low-cost inspection tools and protocols explored by the team fared no better. Higher levels of nitration were found to correlate with relatively lower deflagration temperatures, but correlations between visual observations and measured nitration were poor, making it impossible to deduce flammability from observed physical condition. The brown powder samples proved insensitive to ignition by impact and friction, according an international standard for the transport of hazardous materials. Against the caveat that we have tested a limited number of brown powder samples with only partially known provenance, we conclude that brown powder is non-hazardous on the basis of our dataset. An unexpected finding from our accelerated aging trials is that 80 % relative humidity (RH) aging conditions lead to the fastest degradation of the image carried by nitrate film, without significantly decreasing its combustibility. The 30 %RH aging conditions lead to better image preservation, yet our samples tended to depolymerize into a sticky liquid. However, the intermediate 50 %RH aging condition lead to better image retention and the degradation of the film into a significantly relatively non-hazardous byproduct.

Avenues for Future Research & Advocacy

Looking forward, a number of scientific questions remain. First, there is the question of how provenance affects the observed decomposition modes and mechanisms. Future work might employ our same testing protocols on a wider array of cellulose nitrate film stock samples, in order to assess and to establish the generality of our findings. There are also unanswered questions about the role of storage cans in facilitating nitrate deterioration, especially, due to the trapping of evolved gases therein and the potential role of iron in catalyzing decomposition. In recognition of the quantity of the material in cultural heritage holdings, future research on cellulose nitrate should include studies of sheet film. Finally, further translational work and original research is required to develop pragmatic practices for archivists, conservators, and safety officials.

Introduction

This project originates from an awareness that cellulose nitrate-based motion picture film stock—that is, nitrate film—is highly flammable and is prone to physical deterioration over time. Most movies made before the early 1950s used nitrate film stock, and original prints from the era that survive in film archives or private collections are subject to chemical decomposition and pose significant fire risks. In addition, because of its chemical structure, as nitrate film decomposes, it typically releases toxic gases that pose threats to human health. These general characteristics have been known for some time. However, research conducted by Dr. Heather Heckman, the Director of Moving Image Research Collections at the University of South Carolina, revealed that specific, reliable knowledge about nitrate film stock’s behavior is lacking, or at best, inconsistent. In her article “Burn After Viewing, or, Fire in the Vaults: Nitrate Decomposition and Combustibility” (*The American Archivist*, Winter 2010), Heckman reported that the safety regulations governing nitrate storage, shipping, and handling, and the best practices employed by archivists are based on research that is sometimes contradictory or inconclusive.

The purpose of the Wisconsin Nitrate Film Project was to determine the physical and chemical conditions that might account for these vexing qualities of nitrate film. It was Dr. Heckman’s idea to undertake this project and to launch a joint venture among The Wisconsin Center for Film & Theater Research, the Mahanthappa Research Group in the Department of Chemistry at the University of Wisconsin–Madison, and the Wisconsin Historical Society. The participants sought to understand the chemical processes by which nitrate decomposes and to ascertain whether deteriorated nitrate film stock is more dangerous than nitrate stock in good condition. The scientific aspects of this project were complemented by research on the history of nitrate storage and handling, including surviving information about storage problems. The project also involved the collection of information from modern professionals who deal with the practical aspects of nitrate film preservation, handling, projection, and transportation.

The project tasks were naturally divided between a group focusing on the physicochemical processes underlying the degradation of nitrate film and its flammability, and a group who studied current and historical practices for the archival storage and handling of nitrate films and the discourse surrounding these practices. Activities in the chemistry group were led by Professor Mahesh Mahanthappa, then a faculty member in the Department of Chemistry at UW–

Madison. (Professor Mahanthappa has since moved to the University of Minnesota–Twin Cities Department of Chemical Engineering and Materials Science.) He conducted the chemical studies of heritage nitrate film at UW–Madison in conjunction with three graduate student research assistants in Materials Chemistry: Glen B. Thomas, Milton H. Repollet–Pedrosa, and Allen Wang. Working with the history and conservation groups was Vance Kepley, Professor of Communication Arts at UW–Madison and then Director of the Wisconsin Center for Film & Theater Research (WCFTR). Conservation and historical research colleagues were: Katie Mullen, Preservation Coordinator at the Wisconsin Historical Society; Mary Huelsbeck, WCFTR Assistant Director; Maxine Ducey, WCFTR Film Archivist (for earlier stages); and Amy Sloper, WCFTR Film Archivist (for later stages). The primary research assistant for historical and conservation research was Amanda McQueen, a Film Studies Ph.D. candidate in the Department of Communication Arts. In fall 2014, her duties were assumed by fellow Film Studies graduate student F. Booth Wilson. The undertakings of the history and conservation delegation included formulating and testing a physical inspection process for nitrate film samples; developing an extensive annotated bibliography on nitrate film that would encompass popular, scientific, conservation, safety, and historical literature; developing and executing a survey of members of the archival community; and organizing a series of oral histories with veteran professionals who have worked extensively with nitrate film.

The experimental progress of the Wisconsin Nitrate Film Project was reviewed throughout by an advisory board comprised of three archival professionals: Douglas Nishimura, Research Scientist at the Image Permanence Institute; Mike Pogorzelski, Director of the Academy Film Archive; and Ed Stratmann, Associate Curator at George Eastman House. Heather Heckman, Director of Moving Image Research Collections at the University of South Carolina and the creator of the grant project, also served in an advisory capacity.

This white paper summarizes a number of the major initiatives undertaken during the course of this project: the survey sent to archival institutions; the chemical and physical testing of cellulose nitrate samples, and—more briefly—our development of an annotated bibliography, an oral history, and a project website. We also discuss our interactions with the National Fire Protection Association and outline avenues for future research and advocacy.

In addition to disseminating our findings via the Nitrate Website and future peer-reviewed publications, we will also make research data and documentation generated over the course of the Wisconsin Nitrate Film Project available for free download through Minds@UW.

We acknowledge direct financial support for this work from the National Endowment for the Humanities. This work also utilized central facilities at the University of Wisconsin–Madison funded in part by U.S. National Science Foundation grants for mass spectrometry (CHE-9974839), NMR spectroscopy (CHE-1048642) and supplementary gift funds from Paul J. Bender, the UW-Madison NSEC (DMR-0425880 and DMR-0832760), and the CEMRI (DMR-0520527 and DMR-1121288). We also acknowledge infrastructure and additional financial support from The Graduate School of the University of Wisconsin–Madison.

Survey of Contemporary Archival Practices

1. Survey Background and Objectives

In the fall of 2013, the conservation and history groups created a survey to examine the gap between actual practice and prescriptive regulations among archives holding cellulose nitrate based collections. We developed questionnaires (one for each survey population, discussed below) that focused on determining the type of archival institution; the size of the nitrate collection at that institution; the institution's day-to-day practices for nitrate storage, handling, and shipping; and the knowledge or experience of nitrate held by that institution's personnel. Questions took into account both common archival practices that are not accounted for in cellulose nitrate related regulations but that are employed as preservation methods (such as the use of freezers for long term storage of film based materials), and also took into account prescribed practices (such as the use of NFPA 40-complaint vaults for long term storage of nitrate film). In particular, we wanted to learn about awareness of and adherence to regulations pursuant to the National Fire Protection Association (NFPA), which deals with life safety issues related to the storage and use of nitrate film; health and safety issues for workers dealing with deteriorating film, potentially subject to Occupational Health and Safety (OSHA) regulations; transportation and shipping regulations, governed by the U.S Department of Transportation for ground transport and by the International Air Transport Association (IATA) for air transport; and hazardous materials disposal of nitrate film, regulated by the U.S. Environmental Protection Agency (EPA). A copy of each questionnaire can be found in Appendix 1.

The regulatory practices can be difficult and costly for archives to meet, and perhaps in some cases, pragmatically impossible for an archive to achieve. Because of this, we sought information about the levels of awareness and regulatory compliance in two distinct types of archive. First, the specialty motion picture archives which have an emphasis on nitrate film preservation, and which are presumably representative of an experienced and nitrate user group. Second, U.S. state government and territorial archives, which are tasked by local statutes with preserving certain government records indefinitely, some portion of which can be nitrate film based motion pictures or photographic negatives. These archives are presumably representative of institutions with fewer resources to devote to the special concerns of nitrate film. Our two constituent populations were represented by the members of the Nitrate Committee of the Association of Moving Image Archivists (AMIA) and the Council of State Archivists (CoSA), respectively.

2. Survey Methods and Populations

The AMIA survey was conducted through the University of Wisconsin's Qualtrics survey hosting service and an invitation to participate was disseminated to members of the AMIA Nitrate Committee through use of their listerv, which has about 100 members. Membership on the committee is open to all interested members of the larger AMIA association, which includes individual collectors, historians, and filmmakers as well as archivists. We sought, and received, responses to the survey through this committee at the institutional level (i.e., one survey represents one film archive), but the total number of institutions represented by the committee is unknown.

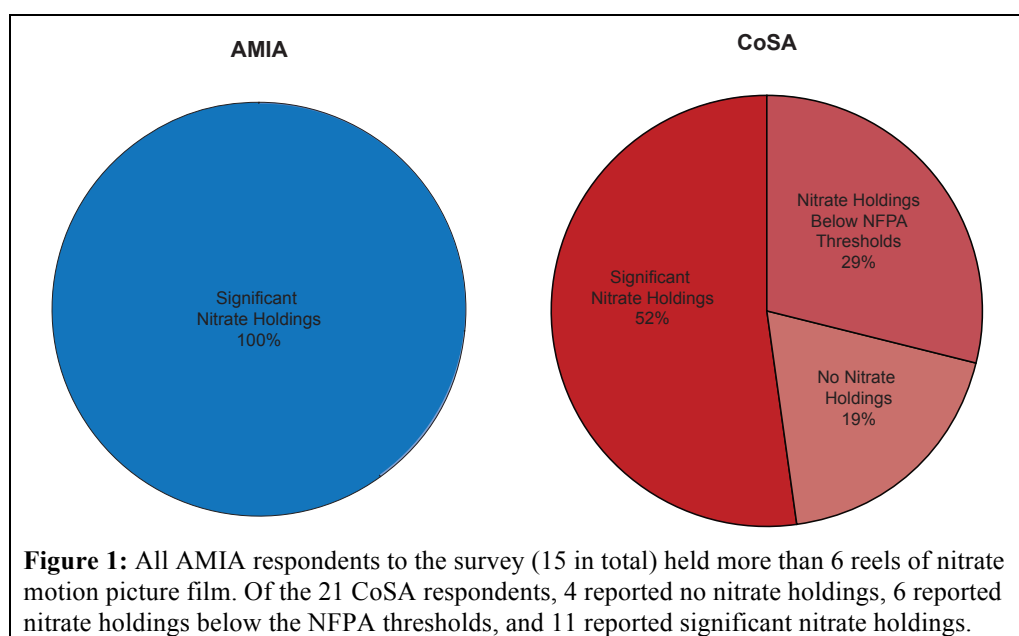
The Council of State Archivists has 56 members, each representing one U.S. State or Territorial archive. The survey questionnaire was distributed by email to each member by CoSA executive director, Anne Ackerson, who tabulated the raw data into an excel spreadsheet.

We received 15 responses from members of AMIA (presented in blue in the graphs below) and 21 responses from members of CoSA (presented in red). A list of the respondents from the two constituencies, with identities redacted, can be found in Appendix 1.

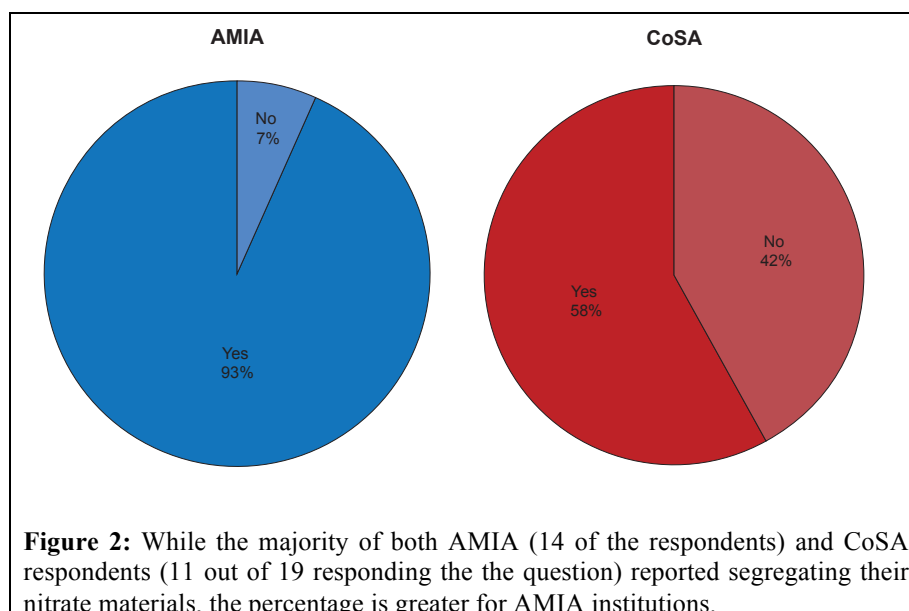
While we have made some preliminary inferences based on the survey data, and have for pragmatic reasons, drawn comparisons between the two populations in our discussion of the results, the caveat must be made that a larger population and more rigorous methodology must be employed before statistically significant conclusions could be drawn.

3. Survey Results

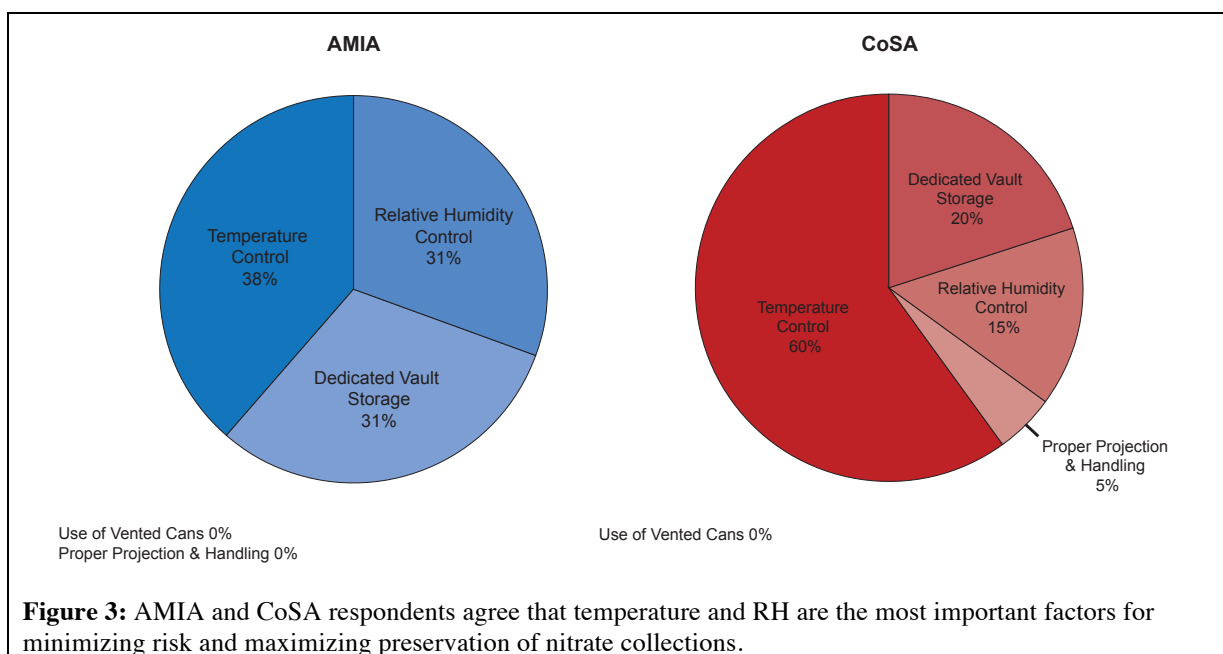
Participants were asked to report the quantity of their nitrate holdings. AMIA Nitrate Committee members were asked to report the number of nitrate motion picture film holdings, while CoSA participants were asked to report on nitrate motion picture film as well as nitrate sheet film holdings. “Significant” amounts are defined in our results as holdings above six 1000 foot reels, 4 cubic feet of sheet film, or a combination of both. These amounts are considered “significant” because they would be subject to the requirements for long term vault storage outlined in NFPA 40, the Standard for the Storage and Handling of Cellulose Nitrate Film, in states which have adopted this standard. Figure 1 presents the data regarding the nitrate holdings of the surveyed institutions.



As a very simple measure of the level of attention which can be given to nitrate holdings, participants were asked, “Is nitrate film segregated from other materials?” Segregation could potentially result from NFPA compliant storage schemes, or could be a preventative preservation



measure undertaken, for example, to prevent cellulose acetate film collections from undergoing degradation due to nitric acid exposure. As shown in Figure 2, it is common practice across all types of repositories to segregate nitrate materials from the rest of the collection; however, 93% of AMIA versus only 58% of CoSA respondents reported this practice as a basic preventive measure.

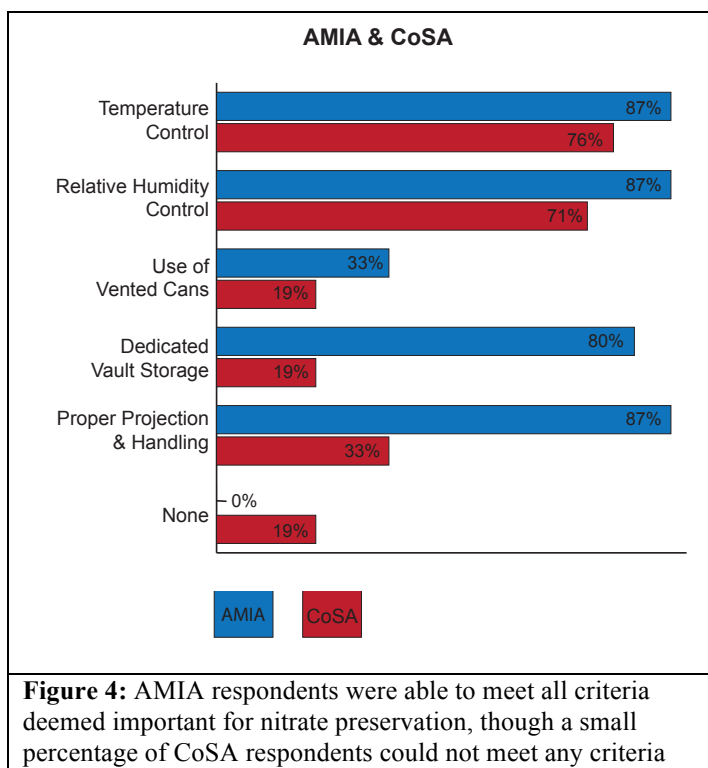


Participants were given a list of five factors which are commonly held or reported in the literature to play a role in minimizing risk and maximizing preservation for nitrate film. They were asked to rank them, on a scale of 1 to 5, from most important to least important. The five factors are temperature control, relative humidity control (RH), use of vented cans, dedicated vault storage, and proper projection and handling. As indicated Figure 3, a plurality of the 14

AMIA respondents to this question (38%) and the majority of the 20 CoSA respondents (60%) stated that temperature control was the most important factor. Among the rest of AMIA respondents, 31% claimed RH was most important and 31% claimed vault storage was the most important. Of the CoSA respondents, 20% said that vault storage was most important, 15% said RH was most important, and 5% said proper projection and handling was most important. Both AMIA and CoSA respondents selected RH as the second most important factor, but AMIA respondents were more divided over whether RH or temperature were more important. Table 1 compares the rankings for all five factors between the two constituencies.

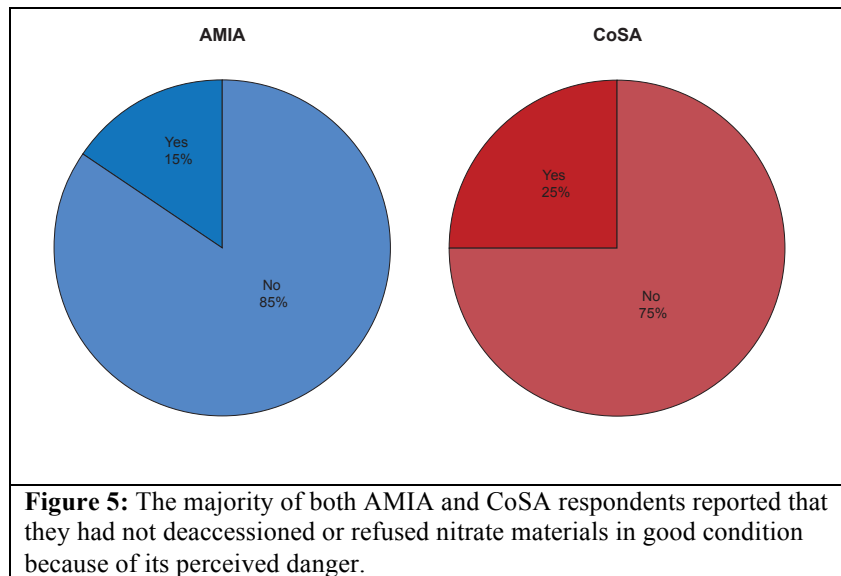
Table 1: Please rank the following (on a scale from 1 to 5) in terms of what you understand to be the most important conditions for minimizing risk and maximizing preservation for nitrate film.

	AMIA	CoSA
Most	Temperature Control (38%)	Temperature Control (60%)
2nd	Relative Humidity (31%) / Temperature Control (31%)	Relative Humidity Control (55%)
3rd	Dedicated Vault Storage (54%)	Use of Vented Cans (45%)
4th	Proper Projection & Handling (54%)	Dedicated Vault Storage (40%)
Least	Use of Vented Cans (62%)	Proper Projection & Handling (75%)



However, it should be noted that while the majority of CoSA respondents reported being able to meet those criteria deemed most important—temperature control (76%) and relative humidity control (71%)—19% of CoSA respondents reported that they were not able to meet any of the necessary storage conditions. The majority of AMIA respondents (80% or more) reported being able to meet all of the criteria, with the exception of vented cans (see Figure 4). Given that many AMIA respondents thought vented cans were the least important factor, these data might reflect a decision not to use them, rather than an actual inability to secure them. It should also be noted that vented cans may not be of concern to CoSA respondents who might hold only significant quantities of nitrate sheet film, rather than nitrate motion picture film.

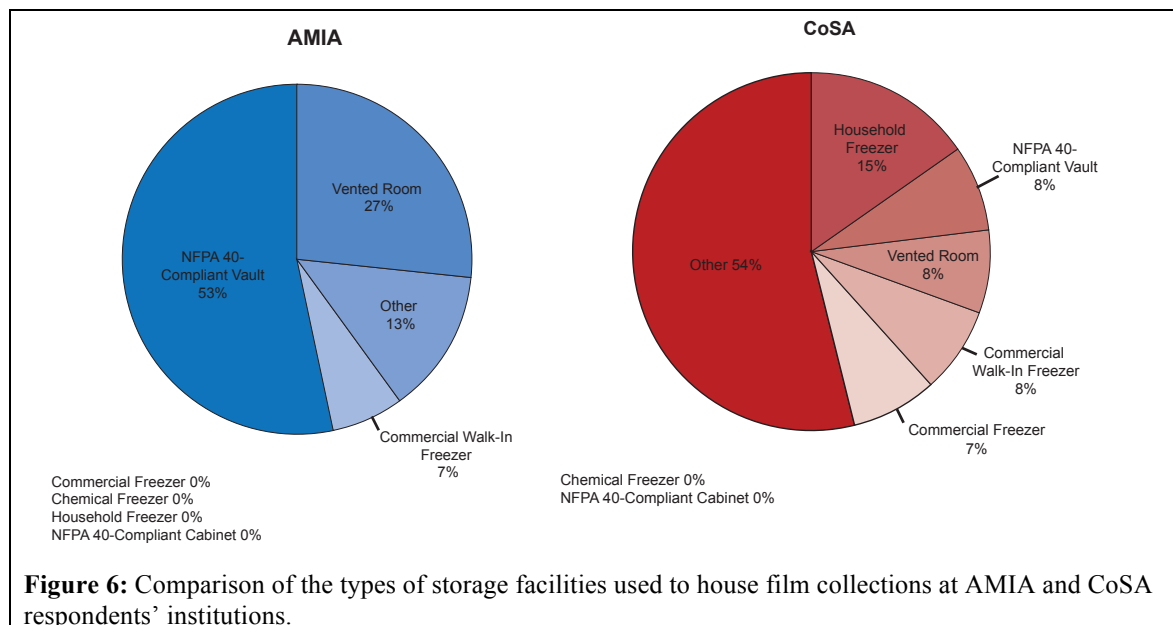
When asked “Has the perception of nitrate film as dangerous or the difficulty of dealing with regulations caused you to not accept or deaccession nitrate film in good condition,” the majority of both AMIA and CoSA respondents—85% and 75%, respectively—reported no, they had not (see Figure 5). Perhaps reflective of the lack of perception of nitrate’s danger—as evident in Figure 5—experience with nitrate fires was rare among all respondents. Five out of fourteen AMIA respondents to the question “Have you had any direct experience with nitrate fires,”



answered affirmatively. Of these five, three reported experience with a deliberate burn for educational or disposal purposes only. Two out of twenty respondents from CoSA reported direct experience with a nitrate fire. The majority of respondents to both surveys, however, reported that they had witnessed nitrate in their collections deteriorate.

Comparing answers from the two groups, however,

also revealed significant divergences in terms of storage and preservation practices. For instance, AMIA and CoSA representatives were asked to select the type of storage facility used to house their film collections based on common options: household freezer, commercial freezer, commercial walk-in freezer, chemical freezer, NFPA 40-compliant vault, NFPA 40-compliant cabinet, vented room, or other. It is notable that the majority of AMIA respondents (53%) identified a dedicated film vault, while only 8% of CoSA respondents mentioned the equivalent. The CoSA respondents sometimes listed multiple options, and 54% described their storage facility as “Other” (see Figure 6). Given the percentage of CoSA respondents with “significant holdings”—which would trigger NFPA 40 compliant storage requirements—these results suggest that there are obstacles achieving regulatory compliance for this community.



Because we anticipated that CoSA respondents might have fewer resources than the AMIA nitrate community to devote to the special concerns of nitrate film, CoSA participants were

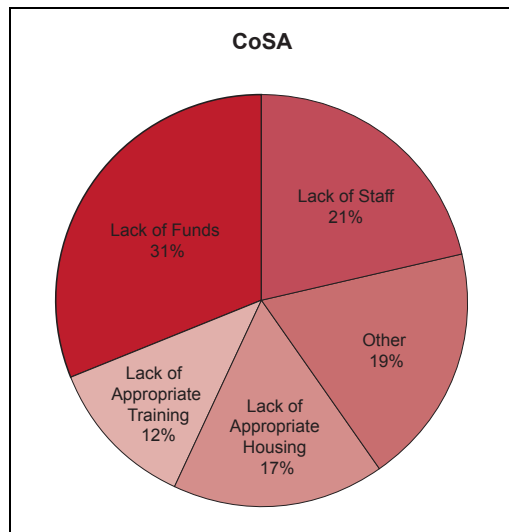


Figure 7: CoSA participants answer the question “What are the obstacles to overcome for management and care of nitrate film in your institution’s collection?”

asked to identify obstacles in caring for their nitrate holdings, as shown in Figure 7. The most commonly reported obstacles were lack of funding and staff. Lack of appropriate training for staff was the least commonly cited reason.

In an effort to gauge compliance efforts and awareness of the varied regulations concerning nitrate film, respondents from both communities were also asked which regulatory agencies may have influenced their institutional policies on nitrate storage, handling, or shipping. Specifically, they were asked to select from the following list: National Fire Protection Association (NFPA), the Occupational Safety and Health Administration (OSHA), the International Air Transport Association (IATA) and the Department of Transportation (DOT), the Environmental Protection Association (EPA), and/or other International or Non-

American organizations. As shown in Figure 8 below, the AMIA delegation reported a greater variety of relevant agencies and a higher level of regulatory influence.

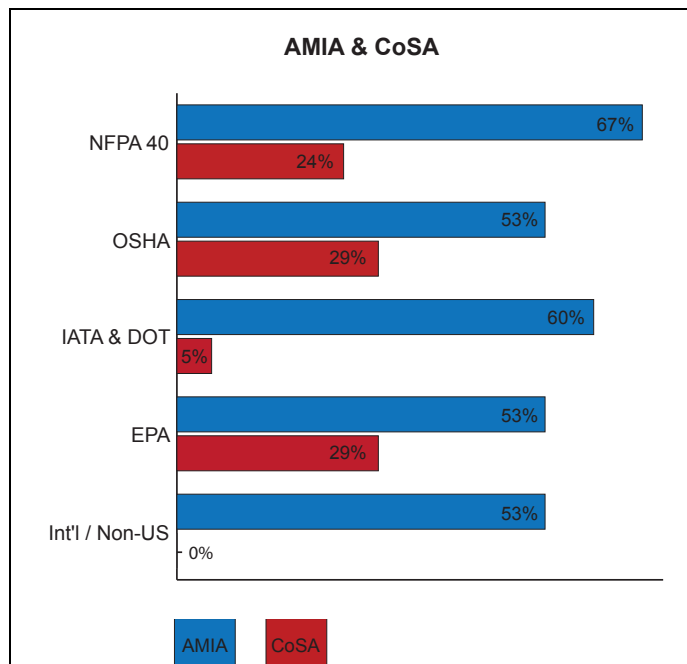
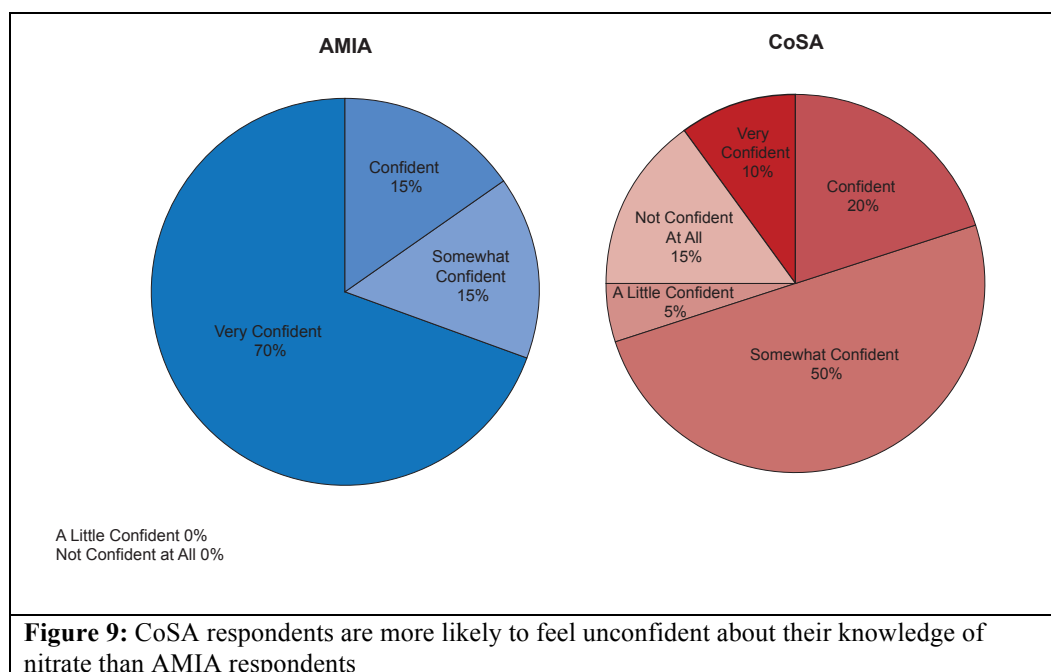


Figure 8: AMIA respondents reported a higher level of regulatory influence regarding the storage, shipping, and handling of their nitrate collections.

Similarly, AMIA respondents reported more experience with and training in the shipping of nitrate materials, while very few CoSA respondents reported receiving training. Moreover, while both AMIA and CoSA respondents cited books and articles and on-the-job-training as the chief methods of learning about nitrate, AMIA respondents were more likely to have learned about nitrate while attending university.

Most significantly, perhaps, respondents had the opportunity to self-report on their level of confidence in their knowledge of nitrate. As shown in Figure 9, all respondents from the AMIA group selected “somewhat confident,” “confident,” or “very confident.” However, while a majority (80%) of the CoSA group felt “very confident,” 15% felt “not confident at all” about their knowledge of nitrate.

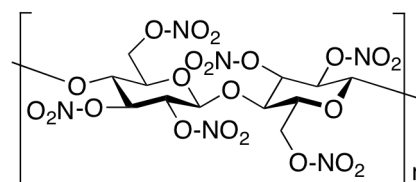


Our survey results thus highlight the different levels of experience and knowledge between these two different groups of archivists, and suggest that the non-specialist archival community represented by CoSA would particularly benefit from educational and funding opportunities to assist in the care of nitrate holdings. The full results of the survey with additional data and analysis can be found in Appendix 1.

Chemical and Physical Testing of Cellulose Nitrate Samples

Introduction

At a fundamental level, the degradation of heritage nitrate film is a polymer degradation process whereby cellulose nitrate undergoes a series of chemical decomposition reactions that lead to noticeable changes in the physical properties of the material. Cellulose nitrate is intrinsically an unstable material that decomposes by a combination of hydrolysis of its constituent nitrate esters and by reactions that cleave the polymer chains into lower molecular weight species. We use polymer characterization techniques to elucidate changes in cellulose nitrate film and to identify how these transformations affect its flammability properties. This report has a specific emphasis on understanding its flammability properties. Other related efforts are discussed in separate efforts:



Cellulose Nitrate

polymer chains into lower molecular weight species. We used a suite of chemical analysis and polymer characterization techniques to elucidate changes in the chemical structure of cellulose nitrate film and to identify how these transformations affect its physical properties, with a specific emphasis on understanding its flammability profile. In this section, we describe four separate efforts:

1. Visual analysis methods employed to examine film samples used in subsequent chemical testing and accelerated aging protocols, in order to discern correlations between physical appearance of heritage nitrate film and its chemical condition,

2. Quantitative physicochemical characterization of nitrate film samples in varying states of decay, as described by the qualitative—yet useful—five-stage model of cellulose nitrate deterioration commonly employed by archivists,
3. Experimental studies of the accelerated aging of samples of a pristine, deaccessioned nitrate film from 1935 (Stage 0) under elevated temperature conditions at varying relative humidity levels and subsequent analysis of their chemical characteristics, and
4. Assessments of the shock- and friction-sensitivity of four different “brown powder” samples, which arose from the decay of heritage nitrate film under archival conditions using best practices for its handling.

These studies were specifically motivated by a pressing need to understand how nitrate film degrades and whether or not its degradation products are dangerous, findings which would aid in the development of practices for the successful yet safe preservation of these flammable artifacts of our cultural heritage.

1. Sample Origin and Sample Size

One of the difficulties of conducting research on cellulose nitrate is the lack of available of samples. The methods of analysis required to study nitrate’s chemical behavior require destruction of the film, yet the bulk of nitrate films held in archival collections are rare and unique historical artifacts. Following a review of its film holdings in 2010 and 2011, however, the conservation staff at the Wisconsin Center for Film and Theater Research (WCFTR) and the Wisconsin Historical Society (WHS) deaccessioned a number of reels of 35mm nitrate film and, agreed to donate seven of them—all manufactured by Eastman Kodak prior to 1951—to this project, instead of disposing of these materials to mitigate perceived fire risks. This action provided us with the primary sample materials on which we performed our chemical analysis.

In selecting which of the deaccessioned films to subject to a comprehensive battery of physical and chemical testing, we were guided by the five-stage process of decay commonly used by archivists when assessing their nitrate collections. As described by the National Film Preservation Foundation’s *Film Preservation Guide*, this process is as follows:

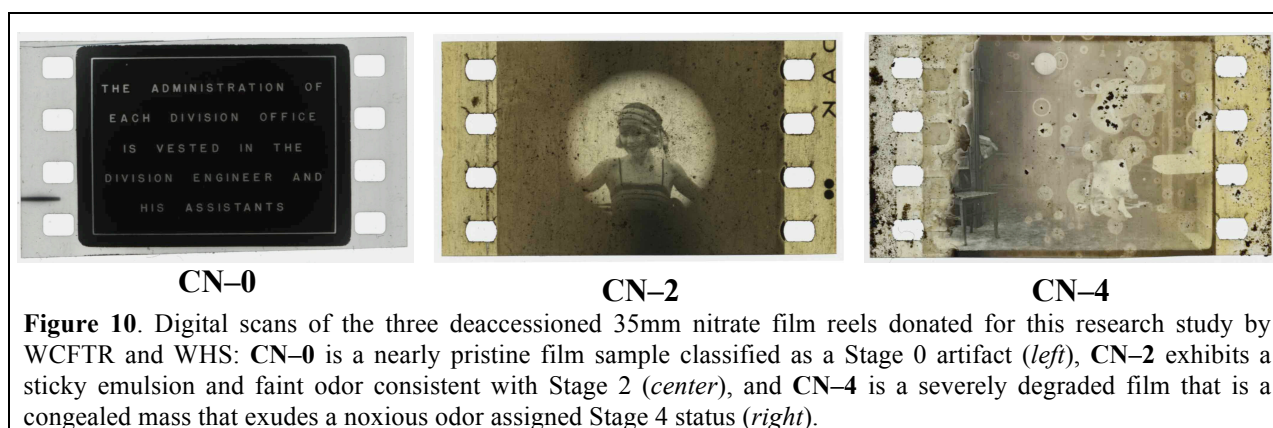
- Stage 0: Film exhibits no signs of decay
- Stage 1: Image fading. Brownish discoloration of emulsion. Faint noxious odor.
- Stage 2: Sticky emulsion. Faint noxious odor.
- Stage 3: Emulsion softens and blisters with gas bubbles. More pungent odor.
- Stage 4: Film congeals into a solid mass. Strong noxious odor.
- Stage 5: Film disintegrates into a brownish power.

For the most part, this five-stage process is described consistently across the literature on nitrate film, but there are some inconsistencies. Most significantly, while the majority of sources claim that combustibility increases in the latter stages of decomposition, a few—such as the International Standard, *ISO 10356: Cinematography – Storage and Handling of Motion Picture Films*—assert that films in Stage 4 or Stage 5 are actually less dangerous. Furthermore, these stages are not correlated with any concrete timeline, giving archivists little guidance in determining how quickly a film will reach Stage 5 once it has started to decay. Therefore, given

the centrality of the five-stage process to archival practice and the disparities that exist in how this process is described, we decided to use these stages as our starting guidelines for sample selection.

By running chemical tests on samples in different stages, we hoped to determine whether this visual classification process actually correlates with severity of decay and combustibility. Of the available deaccessioned film reels, we selected three representative samples that reflected a wide variety of conditions (see Figure 10).

- **CN-0** is dated from 1935 (Kodak +■) and is in nearly pristine condition. According to the 5 Stage model, it is best described as Stage 0. This reel, labeled “Wisconsin Highway Film Titles,” consists of intertitles describing highway construction and administration.
- **CN-2** is dated 1919 (Kodak ••) and exhibits the yellowing of the base, slightly sticky emulsion, and faint noxious odor characteristic of Stage 2 of decomposition. With the aid of the Library of Congress, we have identified this film as *Chickens in Turkey* (1919), a two-reel comedy starring Dorothy Earle and Marcel Perez.
- **CN-4** is dated 1919 (Kodak ••) and large portions of this reel had congealed into a malodorous, yellow mass, as is characteristic of Stage 4 of decomposition. It is possible that this is the second reel of *Chickens in Turkey*.



The dates ascribed to these samples derive from a combination of the edge codes printed on the film stock (given above in parentheses and visible on the image for **CN-2** in Figure 10), and provenancial information from WCFTR and WHS. The year refers to when the stock was manufactured, not when the motion picture was produced.

Although this is a rather small sample size, it is comparable to previous investigations of nitrate decomposition. Single, consecutive frames from each of these three reels were cut and prepared for testing. While the condition of the film on **CN-0** and **CN-2** was relatively uniform, the quality of the film on **CN-4** varied from one point to another. That is, while portions of the reel were congealed and completely devoid of emulsion, others were in relatively good condition. When selecting individual frames from our **CN-4** sample for analysis, then, we chose those that were comparable in terms of their stage of decay, rather than taking them consecutively from the reel. In total, we tested approximately 115 frames of the **CN-0** film, and approximately 45 frames of the **CN-2** and **CN-4** films.

For the BAM Fallhammer and BAM Friction tests, which were conducted by the safety services firm Chilworth Global (*vide infra*), we obtained four samples of Stage 5 degraded brown powder from two geographically diverse major film archives (who wish to remain anonymous). Three of these samples are depicted in Figure 11.



Figure 11. Brown powder samples donated from geographically diverse major archives were collected for physical properties testing, including friction and shock sensitivity tests.

Having determined which samples we would use, we began our chemical analysis. Starting in March 2012, the laboratory group designed and executed a series of experiments to test some of the assertions commonly found in extant literature about cellulose nitrate film. These tests, described below, provided some initial information about the chemical behavior of cellulose nitrate that we could use to inform the parameters of our subsequent 360-day accelerated aging trial that began in March 2013.

2. Visual Inspection and Analysis as a Means of Determining Chemical State of Decay

In conjunction with the accelerated aging trial, the conservation group conducted a physical inspection project. This component was designed to determine whether there are correlations between the chemical behavior of the film, as indicated by the results of our chemical analysis, and what we can see and measure on the film stock with the naked eye and simple tools. We hypothesized that if we could determine that such correlations exist, archivists and conservators would be then able to determine the stability of their nitrate holdings using tools readily available to them and techniques that do not require sophisticated knowledge of chemistry or destructive testing.

We performed this physical inspection only on the film samples used in the accelerated aging trial described below. The results were documented according to the scoring sheet developed by the conservation group, given in Appendix 2. All the frames were also scanned in order to establish a good visual record of their appearance. Representative scans are shown in Figure 10.

The first step in the physical inspection process was to measure the density of each frame using a densitometer. We measured the lightest and darkest portion of the image, and also recorded the density of the emulsion-free area around the sprocket holes. This could help us quantify both the fading and decay of the image, but also the yellowing of the base. We then measured the thickness of each frame using a micrometer.

Next, we examined the sample for evidence of physical damage—anything that altered the condition of the base of emulsion of the frame. We rated various parameters of the frames' physical condition on a scale of 0 to 3, based on the severity of the damage or how much of the frame was affected:

- 0 = No damage
- 1 = Light damage — less than 1/3 of frame affected
- 2 = Moderate damage — 1/3 to 2/3 of frame affected
- 3 = Heavy damage — more than 2/3 of frame affected

Our ratings were also influenced by comparisons with the samples from Reel 1, as this film was in near perfect condition and thus provided a baseline. By gently flexing the frames, we tested the cellulose nitrate base for brittleness or softness; a frame that did not seem at all brittle or soft would be rated 0, while a frame that was extremely brittle or overly soft would be rated 3. We then examined the frames visually for yellowing of the base—indicated by selecting “Yes” or “No” on our inspection sheet—and fading or bleaching of the emulsion, which was rated based on how much of the area of the frame was affected. Using careful touch, we tested the frames for stickiness; a slightly tacky frame would be rated 1, while a frame that was fused to another would be rated 3. We also examined the frames for buckling—rating 0 for a flat frame and 3 for a heavily buckled frame—and counted the number of tears, folds, and broken sprocket holes. The presence of foreign matter, such as dirt, grease or oil, adhesive residue, or brown powder, was also recorded, rating 0 for a completely clean frame and 3 for a very dirty frame. Using a measured loupe, we then calculated in square millimeters (mm²) how much of the image had disappeared due to decomposition. Finally, we sought to quantify how scratched each frame was. Using a measured loupe and a light source cast along the surface of the film, we counted the visible scratches along two imaginary baselines, one bisecting the frame horizontally and one bisecting the frame vertically. Estimating that each scratch covered about .05 mm² of surface area, we then multiplied the number of horizontal and vertical scratches by .05 to calculate approximately how much surface area of the frame was scratched. This was done for both the base and emulsion sides of each frame. Completed inspection sheets for a Stage 0, Stage 2, and Stage 4 film sample are also given in Appendix 2.

Sample frames were tested in groups of five in the accelerated aging trial, as described in more detail below. As part of the physical inspection process, Katie Mullen, Preservation Coordinator at the Wisconsin Historical Society, selected one frame out of each group of five to be photographed using Reflectance Transformation Imaging (RTI). Developed by Hewlett–Packard Labs, and promoted to the conservation community by Cultural Heritage Imaging (<http://culturalheritageimaging.org>), RTI is a computational photographic method that captures the surface shape and color of an object. Using a stationary digital camera, the object is photographed multiple times. For each photograph, light is projected from a different direction and bounced off of small, reflective spheres, which generates different highlights and shadows.



Figure 12. Screenshots of the RTI viewing software, demonstrating how different placements of the “virtual” light source change the appearance of one of our photographed CN-2 film samples.

Using the RTI viewing software (Figure 12), the series of images is combined to create a three-dimensional, interactive image. By moving the “virtual” light, the user can reveal and examine fine details of the photographed object’s surface. In addition, the RTI software allows for the object’s surface shape and color attributes to be mathematically enhanced, which can reveal information not visible by empirical examination. In our case, as evidenced in Figure 13, these enhancements emphasized not only the presence of scratches and foreign matter on the frames, but also the density of the emulsion creating the image.



Figure 13. Screenshot of the RTI viewing software in which the composite image has been enhanced to emphasize the physical texture of the photographed CN-2 sample frame.

This physical inspection process was completed in March 2013, and the samples were then sent to the chemistry group for the accelerated aging trials.

3. Physicochemical Characterization of Cellulose Nitrate Film Samples

Our initial chemical characterization of the nitrate film samples described above sought to assess the validity of correlations between the five-stage classification scheme for cellulose nitrate condition, the molecular composition of the film, and its ultimate thermal stability. A substantial number of literature sources claim that the combustibility of nitrate films increases in the later stages of decomposition, albeit with a few exceptional references suggesting that flammability actually decreases in advanced states of decay. To assess the validity of these conflicting empirical correlations, we employed five different tools in the study of the three different heritage nitrate film samples described above: (1) the Image Permanence Institute (IPI) Acidity Test for nitrate film, (2) size-exclusion chromatography to correlate the molecular weight of the cellulose nitrate polymeric film base and the attributed stage of decay, (3) elemental analysis by combustion to determine quantitatively the chemical element composition of the film base, (4) proton nuclear magnetic resonance (^1H NMR) spectroscopy of dissolved nitrate film bases (gelatin, or emulsion, removed) to understand their chemical structures, with a specific emphasis on quantifying the nitration level of each sample, (5) thermogravimetric analysis (TGA) to assess the decomposition onset and deflagration temperatures of these samples, and (6) differential water sorption studies to measure water uptake of nitrate film samples. In the following sections, we describe the detailed results of our various analyses. Full descriptions of the experimental procedures, analytical instruments, and analysis parameters used are given in Appendix 3.

3.1 The IPI Acidity Test

Based on previous observations that nitrate film stock becomes increasingly more acidic as it decays by virtue of denitration and other chemical processes (Adelstein et al., *SMPTE J.*, **1995**, 104, 281-291), the IPI established a standardized test for nitrate film known as the IPI Acidity Test. We adopted a variant of this test in which we soaked a 50 mg film sample in 5 mL of deionized water in a sealed container for 24 h at 22 °C to leach any acids into the aqueous solution, after which the pH of the solution was measured using pH paper. The pH, defined as $\text{pH} = -\log[\text{H}_3\text{O}^+]$, provide a direct measure of the acidity of the solution. We conducted IPI acidity tests on film frames taken from **CN-0**, **CN-2**, and **CN-4**. Since water takes up atmospheric carbon dioxide, which renders it acidic, and we did not degas the water prior to use in the IPI acidity test, all of the reported pH values are compared to the pH of a control sample of water. The results of our studies, listed in Table 2, are consistent with the general notion that the pristine film exhibits an undetectable acidity within the resolution of this experimental protocol, and that the acidity of the nitrate stock that exhibits advanced stages of decay increases (pH decreases).

Table 2. IPI Acidity Test Results for Heritage Nitrate Film Samples.

Sample	pH
CN-0	4.8
CN-2	3.5
CN-4	4.0
deionized water (control)	4.8

3.2 Size-Exclusion Chromatography (SEC) Analyses of Heritage Nitrate Molecular Weight:

One commonly held notion is that the level of cellulose nitrate decay is correlated with the molecular weight of the film base, since polymer backbone scission by acid-catalyzed cleavage is known to be one possible degradation pathway. One would expect such scission events to decrease the mechanical stability of the film, leading to the embrittlement typified by Stages 4 and 5 of nitrate deterioration. Stimulated by this idea, we sought to quantify the molecular weights and molecular weight distributions of the film base using a well-known methodology in polymer science.

Size exclusion chromatography (SEC) is analytical method that enables quantitative determination of the mean molecular weight and breadth of distribution of molecular weights of a polymer sample. This method relies on a separation of the polymer chains based on their hydrodynamic volumes—that is, the size of the constituent polymer chains upon dissolution in a good solvent. SEC separation is achieved by passage of a dilute polymer solution through a separations column comprising porous gel beads having a variety of pore sizes under a constant flow of fresh solvent. The polymers are thus sieved according to their solvated size (see Figure 14): polymer chains that are too large to enter into the gel are excluded and exit the separations column first, while lower molecular weight polymers

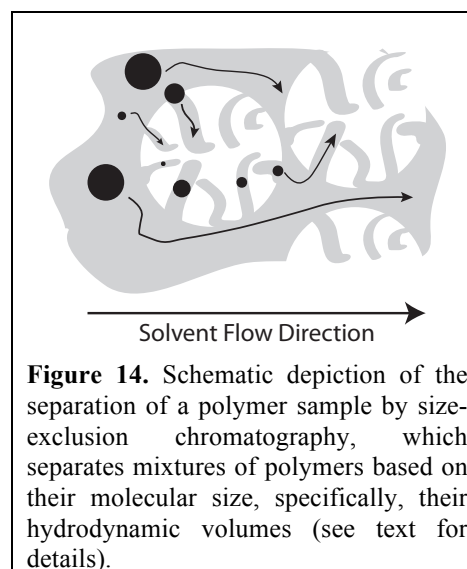


Figure 14. Schematic depiction of the separation of a polymer sample by size-exclusion chromatography, which separates mixtures of polymers based on their molecular size, specifically, their hydrodynamic volumes (see text for details).

pass through the gel at a slower rate and elute later. By monitoring the concentration of polymer in solution exiting the columns as a function of time, one can measure the molecular weight of the polymer and its molecular weight distribution against some calibration reference standard. Typical calibration standards for SEC analyses of chemically-substituted cellulosic polymers are either poly(styrene) standards in tetrahydrofuran (THF), poly(ethylene oxide) in 0.1 M LiBr in *N,N*-dimethylformamide, or poly(methyl methacrylate) in 0.1 M LiBr in *N,N*-dimethylformamide. Since these molecular weights are calibrated against a standard sample that is not cellulose nitrate itself, we draw only comparisons of the relative molecular weights of the samples that we analyzed, as we are primarily interested in trends in the sample set.

In this study, cellulose nitrate samples were treated with bleach (~4–5 wt% sodium hypochlorite in water) to remove the emulsion layer and thus enable focused analyses of only the nitrate film base. The resulting nitrate base was then dissolved in THF at a concentration of ~1.5 mg/mL, and this solution was eluted through two commercial analytical SEC columns (see Experimental Section in Appendix 3 for details). Using differential refractive index detection, the volume of solvent required to elute each polymer sample completely from the set of two columns was measured, and these elution volumes were converted to molecular weights using a calibration curve based on 10 narrow dispersity, poly(styrene) standard samples.

The results of our initial SEC analyses of the three film samples against poly(styrene) standards in THF are listed in Table 3, wherein M_n is the number-average molecular weight of the sample. From these data, we see that the molecular weight of the film base is not at all correlated with the age of the film nor its level of decay. Therefore, we conclude that film molecular weight is not related to the five-stage condition classification. We speculate that the molecular weight of the nitrate base layer likely varied during the manufacture of each nitrate film batch, as a direct consequence of the variable sourcing of raw materials and the specific manufacturing and processing conditions. From a historical viewpoint, it is important to understand that cellulose nitrate film was already in widespread use prior to the broad acceptance of the notion that high molecular weight polymers existed by the scientific community. Thus, analytical methods for accurate quality control of the molecular weight of cellulose nitrate film based most likely did not exist at the time of manufacture of many nitrate film stocks. As a point of reference, analytical SEC was only invented and first disclosed in 1955—four years after the discontinuation of nitrate film manufacture.

Table 3. Results of SEC Analyses of Nitrate Film Samples

Sample	Molecular Weight, M_n (kg/mol) ^a
CN-0	43.0
CN-2	8.0
CN-4	19.0

^a Number-average molecular weight (M_n) determined by SEC with refractive index (RI) detection in tetrahydrofuran at 22 °C calibrated using 10 narrow dispersity poly(styrene) standards.

We note that previous studies of nitrate film degradation by Edge et al. (*Eur. Polym. J.*, **1990**, 26, 623-630) and Hill and Weber (*J. Res. Nat. Bur. Stand.*, **1936**, 17, 871-881) employed viscometry to assess the relative molecular weights of nitrate film samples exhibiting different degrees of degradation. Measurement of the intrinsic viscosity (IV) using an Ubbelodhe viscometer was a common technique for molecular weight measurement prior to the widespread availability of modern analytical SEC instrumentation. IV provides a gross measure of the overall molecular weight of the polymer, whereas SEC utilizes a separations column to sieve the polymer into its

components, thereby allowing determination of the number average molecular weight and breadth of the molecular weight distribution; the latter quantity is not available from traditional viscometry studies.

Both analytical SEC and viscometry suffer from the important caveat that the quantitative results depend upon the solvent in which the analysis is conducted. More explicitly, if the solvent is not a good solvent for the polymer, the analysis may give an erroneous result. Since cellulose nitrate film samples with varying levels of nitration may not be soluble to the same extent in tetrahydrofuran as a solvent, we report all subsequent SEC analyses in 0.1 M LiBr in *N,N*-dimethylformamide against poly(methyl methacrylate) standards. We again reiterate that we use SEC analyses to draw only comparisons of the relative molecular weights of the various samples to understand trends in our heritage nitrate film artifacts. We again reiterate that we use SEC analyses only to draw comparisons to the relative molecular weights of the various samples to understand trends in our heritage nitrate film artifacts.

3.3. Quantitative Elemental Analysis of Film Samples

Cellulose nitrate is derived from the nitration of cellulose, which is a polymer of glucose containing exclusively β -glucoside linkages. The degradation of cellulose nitrate occurs by two hydrolysis (literally, “cutting by water”) mechanisms: (1) cleavage of the nitrate esters that decorate the cellulosic backbone in a process known as “denitration,” and (2) cleavage of the β -glucoside linkages that comprise the cellulose backbone to yield glucose and low molecular weight, variably nitrated glucose oligomers (see Figure 15). Note that denitration is the reverse reaction of the nitration reaction performed on cellulose to manufacture nitrate film base layers.

Denitration is most likely an autocatalytic process, since it liberates corrosive and noxious nitric acid (HNO_3) that can further catalyze both denitration and β -glucoside cleavage of the polymer chains. Both processes reduce, by different mechanisms, the suppleness and overall mechanical integrity of the film in a manner consistent with advanced stages of materials degradation. Denitration yields a less nitrated cellulose, which can form hydrogen bonds that increase its mechanical rigidity. Chain scission reactions reduce the molecular weight of the resulting polymer, which generally degrades its mechanical performance.

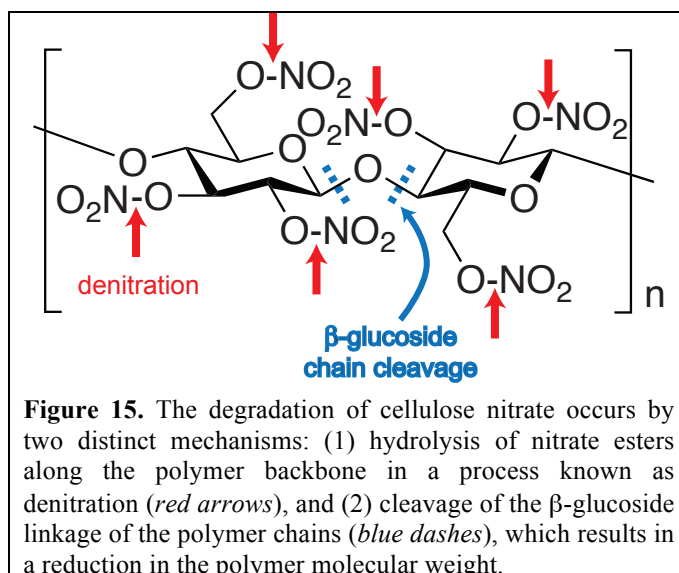


Figure 15. The degradation of cellulose nitrate occurs by two distinct mechanisms: (1) hydrolysis of nitrate esters along the polymer backbone in a process known as denitration (red arrows), and (2) cleavage of the β -glucoside linkage of the polymer chains (blue dashes), which results in a reduction in the polymer molecular weight.

We hypothesized that the five stages of nitrate film deterioration would correlate strongly with the level of film denitration, because the HNO_3 liberated by this process would degrade the emulsion layer of the film by a combination of chemical degradation of the gelatin and oxidation of the silver particles comprising the image in the emulsion layer. One means of testing this hypothesis is to determine the elemental composition of bleached film samples (gelatin

removed). We specifically expected to observe lower nitrogen contents in the more severely degraded film samples.

Controlled combustion of carefully weighed, bleached film samples in the presence of excess oxygen and subsequent quantitative analyses of the liberated gases furnishes one means for assessing the elemental composition of the film samples. Samples were sent to Columbia Analytical Labs (Tucson, AZ) for routine combustion analysis to determine the carbon, hydrogen, nitrogen, and sulfur (CHNS) content of a sample frame from each film reel. Oxygen content was determined by mass balance, based on the initial sample mass. We included sulfur in our analysis, since cellulose nitrate manufacturing typically employed sulfuric acid (H_2SO_4) as a catalyst for the nitration process. However, H_2SO_4 acts as more than a catalyst, as it may become covalently attached to the polymer backbone during the nitration process. While the number of sulfate esters formed in film manufacture is small, the presence of sulfate esters could impact the long-term film stability, since their hydrolysis generates H_2SO_4 that may also catalyze film denitration. The results of our combustion analyses are shown in Table 4.

Table 4. Elemental Composition from Combustion Analysis and Proton Nuclear Magnetic Resonance Spectroscopy

Weight Fraction of Elements Present from Combustion Analysis (C,H,N,S)						Weight Fraction of Elements Present from ^1H NMR Analysis ^a				
Sample	% wt Carbon	% wt Hydrogen	% wt Nitrogen	% wt Sulfur	%wt Oxygen ^b	% wt Carbon	% wt Hydrogen	% wt Nitrogen	% wt Sulfur ^c	% wt Oxygen ^b
CN-0	30.18	3.21	10.97	0.20	55.44	29.55	3.25	11.84	0.20	55.15
CN-2	32.29	3.82	10.38	0.39	53.10	32.34	3.67	11.16	0.39	52.45
CN-4	32.24	3.67	10.03	0.33	53.73	31.96	3.63	11.09	0.33	52.99

^a ^1H NMR analysis was conducted in $\text{DMSO}-d_6$ at 22 °C and spectral assignments derived from Hounslow *et al.*, *Aust. J. Chem.*, **1992**, 45, 627. ^b Oxygen was assumed to comprise the balance of the sample mass in the combustion analysis experiments per convention. ^c Sulfur content used in calculation of the elemental composition of the film derived from combustion analysis.

Supple samples of cellulose nitrate film comprise a combination of cellulose trinitrate (shown in Figure 15) and dinitrate (having two less $-\text{NO}_2$ groups than in Figure 15) repeat units. Lower degrees of nitration of the cellulose backbone were typically less desirable for film applications, due to their relatively brittle nature. For the trinitrate, one expects the nitrogen content of the film to be 13.7 wt%. The dintrate isomer instead contains 12.1 wt% nitrogen. We would have thus expected the nitrogen content for the pristine CN-0 to be bracketed by these two values. However, the nitrogen content was lower than expected for the excellent condition of CN-0. We return to this issue in Section 3.4.

Consistent with our initial hypothesis, the weight fraction of nitrogen in the film samples decreases with increasing stages of decay. While the change in nitrogen content may seem small, this difference is measurable, and its impact on the brittleness of the film sample is readily apparent: CN-4 is much more brittle than the supple CN-0.

3.4. Proton Nuclear Magnetic Resonance (^1H NMR) Spectroscopy Studies:

We also performed solution proton nuclear magnetic resonance (^1H NMR) spectroscopy analyses on gelatin-free film samples (bleach treated to remove the emulsion) dissolved in perdeuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) or perdeuterated acetone ($\text{acetone}-d_6$) at 22 °C. ^1H NMR is a

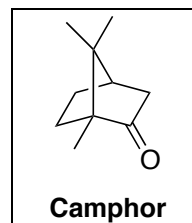
commonly employed chemical analysis tool for determining the structure and atomic connectivity of organic molecules that contain both carbon and hydrogen. Hounslow and co-workers (*Aust. J. Chem.*, **1992**, 45, 627-634) previously reported detailed ^1H NMR spectral assignments for cellulose nitrate in $\text{DMSO}-d_6$ and acetone- d_6 , which allow for identification of the various nitration patterns along the backbone (*e.g.*, trinitration at positions 2, 3 and 6 of the constituent glucose rings *versus* dinitration at positions at 3 and 6, *etc.*). By using our knowledge of the structure discerned from ^1H NMR spectra of **CN-0**, **CN-2**, and **CN-4**, along with quantitative integration of the peaks associated with specific protons along the backbone in the range δ 3.6–5.10 ppm in $\text{DMSO}-d_6$, we calculated the relative amounts of cellulose trinitrate and dintrate present in each sample of film base (Table 5). The nitration level varies in a subtle yet detectable manner, with \sim 2.39-2.46 nitrate functionalities per monomer unit. While the differences in the flexibility of the film appear somewhat inconsistent with these relatively small differences in the nitration of the polymer, the polymer molecular weight may significantly affect the observed mechanical properties. However, it is also possible that the relative brittleness of **CN-2** and **CN-4** arises from different phenomena.

Table 5. Degree of Nitration of Heritage Nitrate Film Samples Determined by ^1H NMR Spectroscopy in $\text{DMSO}-d_6$ at 22 °C

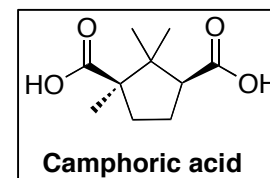
Sample	[dinitrate]:[trinitrate] ^a	Degree of Nitration ^b
CN-0	1.23:1	2.46
CN-2	1.38:1	2.42
CN-4	1.56:1	2.39

^a Determined by quantitative ^1H NMR. ^b Calculated degree of nitration per monomer unit (with a maximum value of three nitrate moieties per monomer).

In the course of the above ^1H NMR analyses of all of the nitrate film samples, we noticed a large number of sharp peaks in the chemical shift range δ 0.5-3.0 ppm that were consistent with the presence of a significant quantity of a small molecule. Detailed analyses of the spectral data enabled assignment of these peaks to camphor. Quantitative ^1H NMR studies indicate that the amount of camphor is as much as 20 wt% in the samples, which accounts for the lower than expected nitrogen content observed by elemental analysis (see Table 4, Section 3.3). Camphor, a terpenoid natural product, was typically added to nitrate film as a plasticizer to increase the suppleness of the film by lowering its glass transition temperature. By accounting for the presence of camphor in the film, we were able to use the ^1H NMR analyses to calculate the relative molar amounts of carbon, hydrogen, nitrogen, and oxygen present in each sample. Using the absolute sulfur content derived from combustion analyses of the samples, we were able to quantify the carbon, hydrogen, nitrogen, sulfur, and oxygen content in an absolute manner. The results of these NMR studies (Table 3) are in good agreement with those expected based on combustion analyses. These findings are also consistent with denitration as one of the major degradation pathways for nitrate film stock.



We note that nitric acid is known to react with camphor by an oxidative ring-opening reaction that yields camphoric acid. Consequently, we suspect that some of the observed peaks in ^1H NMR spectra of the nitrate film base layers may arise from camphoric acid. Due to our inability to resolve the peaks associated with camphor and camphoric acid, we have ascribed all of the observed NMR signals to camphor. The degradation of camphor to camphoric acid reduces the amount of effective plasticizer in the more degraded film



samples, which may conspire with the molecular weight to embrittle **CN-4**. (Camphoric acid is apparently not a plasticizer for cellulose nitrate.) To the best of our knowledge, this degradative reaction of the plasticizer and its impact on nitrate film stability has not been previously documented in nitrate literature.

The presence of camphor in these films is significant for fire protection purposes, since camphor is a highly volatile and combustible solid (vapor pressure of 4 mm Hg at 70 °C or 168 °F). While we do not know the initial camphor content in the film at the time of manufacture, the fact that we could observe ≥ 20 wt% camphor in the film samples suggests its possible role in nitrate base layer flammability. Given its high vapor pressure, it is somewhat surprising that one cannot detect the distinctive odor of camphor when handling nitrate film. Upon abrading the surface of a single **CN-0** film frame with sand paper (320 P grade with an average particle diameter of 642 μm), we noted the smell of camphor emanating from the film. Since abrasion apparently affects the ability of camphor to escape from the film, we attempted to quantify the level of surface abrasion of the film samples with their physical properties as part of our visual inspection project (see Section 2). However, attempts to correlate surface abrasion with the overall condition of the film failed to yield any substantive insights, and further studies along this line of investigation ceased.

3.5. Observation of the Thermal Decomposition of Heritage Nitrate Film by Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a well-known method for studying the thermal stability of polymer samples. In this technique, the mass of a polymer sample is monitored as it is heated at a constant ramp rate (e.g., 10 °C/min) under a flow of oxygen (20 mL/min flow rate) until it fully decomposes, as evidenced by nearly complete mass loss. We assessed the thermal stability of each film sample by analyzing its decomposition profile: the onset of decomposition (T_{decomp} , defined as the temperature at which 5% mass loss is observed) and the deflagration temperature (T_{deflag}) at which the sample combusted. TGA samples were taken from the center of each film frame, which included both the nitrate film base as well as any remaining gelatin (emulsion) layer. Sample TGA traces for **CN-0**, **CN-2**, and **CN-4** are shown in Figure 16. Sample deflagration gave rise to a unique TGA profile, in which bubbling of the emulsion would cause an apparent initial increase in mass, followed by exothermic sample combustion with significant

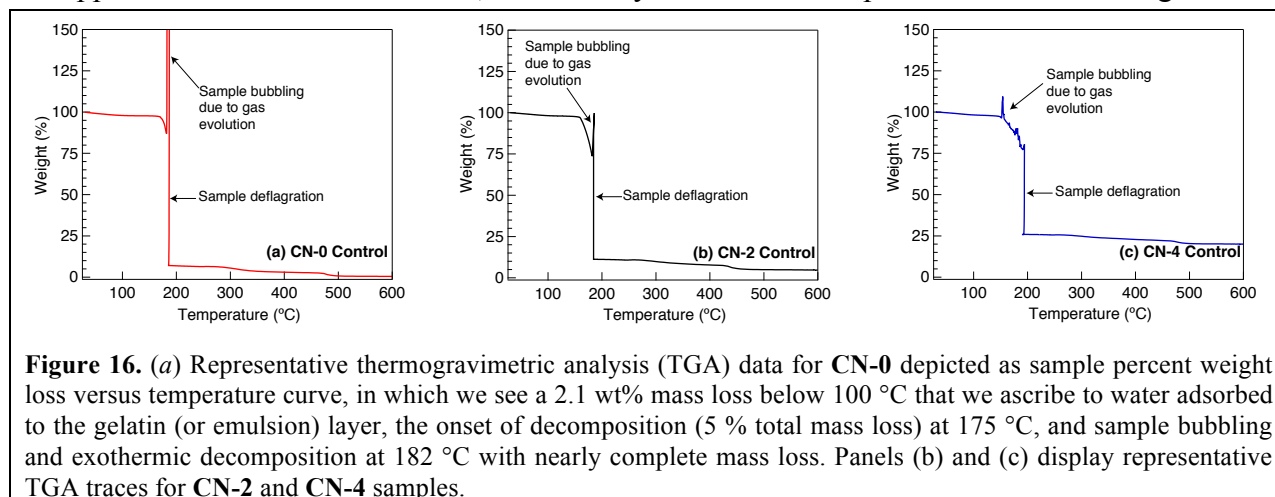


Figure 16. (a) Representative thermogravimetric analysis (TGA) data for **CN-0** depicted as sample percent weight loss versus temperature curve, in which we see a 2.1 wt% mass loss below 100 °C that we ascribe to water adsorbed to the gelatin (or emulsion) layer, the onset of decomposition (5 % total mass loss) at 175 °C, and sample bubbling and exothermic decomposition at 182 °C with nearly complete mass loss. Panels (b) and (c) display representative TGA traces for **CN-2** and **CN-4** samples.

mass loss. Spontaneous sample combustion typically left behind a residue that decomposed at temperatures $T \geq 300$ °C. A summary of the data from these initial TGA analyses of “as is” film samples (prior to accelerated aging) is given in Table 6.

From the data in Table 6, we see that the decomposition onset temperature (T_{decomp}) decreases with increasing stages of decay, as **CN-4** exhibits a T_{decomp} that is ~ 15 °C lower than that of **CN-0**. It is important to recall that this decomposition onset temperature is simply the temperature at which the sample has lost 5% of its original mass—the reasons for the mass loss are not known. The deflagration temperatures of all of the samples are reasonably similar. With the **CN-0** samples, we noted that the surface of the gelatin (image or emulsion) layer developed significant bubbles, consistent with gas evolution from the nitrate base layer (*e.g.*, camphor and nitrogen oxides derived from nitric acid). In order to understand whether the presence of the gelatin (image or emulsion) layer affects the combustibility of the film, we removed the gelatin from the nitrate film stock by brief immersion in 5 wt% NaOCl in water (commercial bleach solution), followed by rinsing with deionized water and air drying. Subsequent TGA analyses of the sample without gelatin exhibited indistinguishable profiles, with complete combustion occurring at ~ 180 °C. Thus, the gelatin layer apparently plays a minor role in the ultimate thermal stability of the nitrate film samples.

Table 6. Summary of Initial Thermogravimetric Analyses of Heritage Nitrate Samples^a

Sample	T_{decomp} (°C) ^b	T_{deflag} (°C) ^c	Notes
CN-0	175 ± 1.6	184 ± 6.6	sample surface bubbles significantly prior to complete combustion
CN-2	156.7 ± 4.5	182.9 ± 4.6	complete combustion
CN-4	152.9 ± 2.8	184.9 ± 5.9	complete combustion
CN-4	155.6 ± 1.9	181.9 ± 1.0	complete combustion
no gelatin			

^a Testing conditions: TGA was run under a 20 mL/min purge of pure oxygen with a ramp rate of 10 °C/min up to 220 °C followed by a jump to 600 °C. Unless otherwise noted, the film samples were tested without removal of the gelatin layer. ^b Decomposition temperature (°C) is defined as the temperature at which 5 % weight loss is observed. ^c Deflagration temperature is defined as the temperature at which the sample completely and exothermically burns (see text for details).

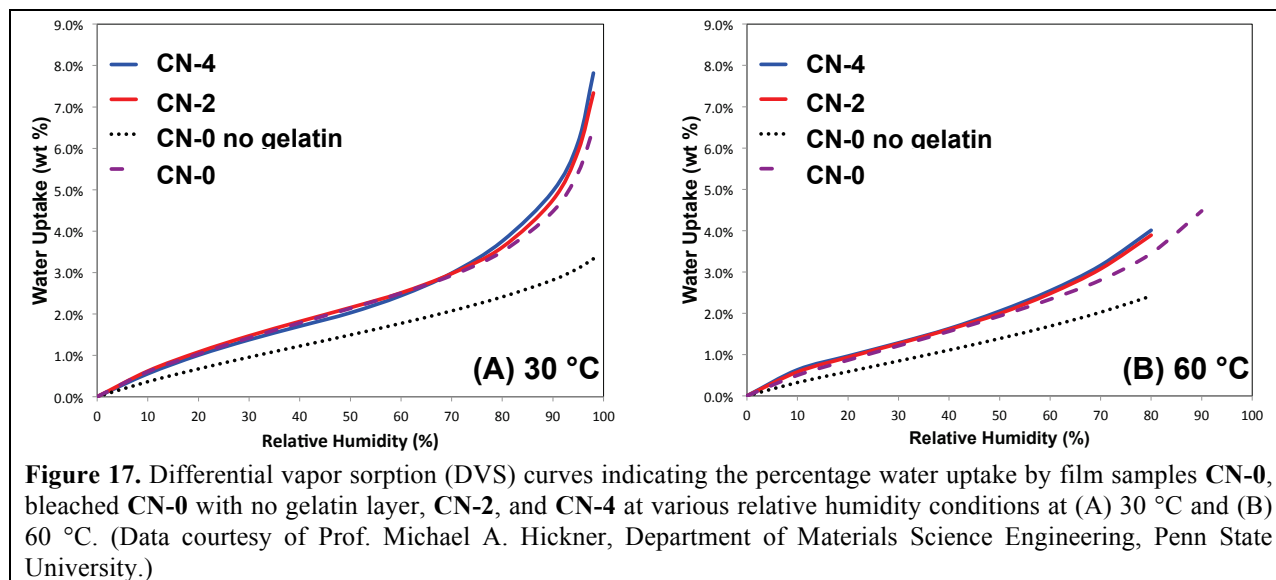
Admittedly, our TGA does not directly mimic the decomposition of nitrate film in a canister within a film vault. A film vault is typically held at constant temperature with modest air circulation, and any gases released by the film remain confined within its storage can and in contact with the film itself. Our thermogravimetric analysis protocol is a dynamic test in which the temperature is raised from 22 °C to some elevated temperature at a constant ramp rate (10 °C/min) under a constant flow of oxygen (20 mL/min), while sample weight loss or decomposition is monitored. To specifically understand nitrate combustibility under the conditions in an archive, one would ideally conduct time-dependent TGA at a fixed temperature of interest (*e.g.*, 30 or 40 °C). To the best of our knowledge, there are no direct nor general correlations between the decomposition and deflagration temperatures measured by dynamic TGA and those arising from the constant temperature time-dependent analyses. We note that the time-dependent studies are extremely time- and resource-intensive, rendering them unwieldy in the context of the large sample set that we sought to survey in our accelerated aging studies. Thus, we utilized the dynamic TGA studies to glean useful information regarding the presence of any volatile compounds in the samples, while also measuring their *relative* flammabilities.

3.6 Differential Vapor Sorption to Quantify Water Uptake by Cellulose Nitrate Film

Since water is a key ingredient in the denitration and hydrolysis reactions that irreparably degrade cellulose nitrate film, we sought to study the water uptake characteristics of these film samples at both 30 °C and 60 °C under a variety of relative humidity (%RH) conditions. In collaboration with Professor M. A. Hickner (Department of Materials Science Engineering at the Pennsylvania State University), we performed differential vapor sorption analyses of **CN-0**, **CN-2**, and **CN-4** film samples. In these experiments, film samples were placed on a sensitive balance and equilibrated in a controlled environment with varying relative humidities. Relative humidity (%RH) is defined as:

$$\%RH = \frac{\text{partial pressure of water vapor}}{\text{equilibrium saturated vapor pressure of water}}$$

By measuring the equilibrium sample mass under each relative humidity condition at a given temperature, we obtained the water uptake curves shown in Figure 17. From these data, we see that the “as is” film samples exhibit water uptake curves that are nearly identical, with 1.3 wt% water uptake at 30 %RH, 2.1 wt% water uptake at 50 %RH, and 4.0 wt% water uptake at 80 %RH at 60 °C. Thus, the water uptake is nearly independent of the condition of the gelatin layer. Upon bleaching **CN-0** to remove the gelatin layer, we observed a noticeable decrease in the water uptake characteristics of the isolated cellulose nitrate base. Unfortunately, this suggests that the gelatin layer holding the image that we wish to preserve acts as sponge that draws water to the film that accelerates its degradation.



3.7 Summary of Initial Physicochemical Studies of Nitrate Film Stability

Our studies up this point indicate that the five-stage classification model accurately correlates with only a few physical and chemical properties of cellulose nitrate films. Increasing stages of decay correlate with lower nitration levels and lower decomposition onset temperatures observed by TGA. However, the five-stage model is not correlated with the molecular weight of the film

base, the amount of camphor present, its water sorption characteristics, nor its deflagration temperature. We note that the water uptake of the film samples primarily depends on whether the gelatin layer is present, but not on its condition. These studies provide only correlations, the origins of which are somewhat unclear. Sample variations due to provenance, manufacturing conditions, and developing conditions likely contribute to the exact physical properties.

3.8 Assessing of the Reliability of Visual Inspection of Nitrate Degradation

Given the data generated by the chemical testing performed on our samples, we were unable to make any quantitative connections between what an archivist can observe visually and the flammability profile of a sample of nitrate film. Thus, we do not believe that our visual inspection process or the use of RTI would be useful to archivists and conservators in ascertaining the potential fire risk associated with their nitrate holdings.

4. Accelerated Aging Studies

Accelerated aging of nitrate film under fixed relative humidity conditions at elevated temperatures have been previously reported by Edge *et al.* (*Eur. Polym. J.*, **1990**, 26, 623-630), Hill and Weber (*J. Res. Nat. Bur. Stand.*, **1936**, 17, 871-881), and Adelstein *et al.* (*SMPTE J.*, **1992**, 101, 336-346; *SMPTE J.*, **1995**, 104, 439-447). These earlier studies focused on the physical and chemical consequences of aging small sample sets (*e.g.*, no more than four distinct samples of variable provenance) at temperatures ranging 50–100 °C under dry air, modest relative humidities, and 95% relative humidity (denoted 95 %RH) for variable lengths of time (typically, less than 50 days). By studying how the properties of the film samples change as a function of aging temperature at various time points, Edge *et al.* and Adelstein *et al.* suggest that the degradation of heritage nitrate film obeys zero order or pseudo-first order Arrhenius kinetics. Under this common reaction rate description, one expects and one observes that the rate of decomposition approximately doubles with every increase in the reaction temperature by ~10 °C. While nitrate film degradation does seem to obey Arrhenius-type reaction kinetics up to 80 °C according to work by Edge *et al.*, changes in the mechanism of decomposition through competing pathways alter the observed kinetics above 80 °C.

Based on these previous studies, we sought to gain deeper insights into the degradation of heritage nitrate films **CN-0**, **CN-2**, and **CN-4** under various relative humidity conditions by accelerated aging under 60 °C for up to 365 days. By studying the physical and chemical properties of the film samples removed from these conditions at various aging time points using visual inspection, the IPI acidity test, SEC, ¹H NMR, and TGA, we sought to understand how storage environments impact the flammability profiles of these materials. The major objective of this study was to understand whether or not nitrate film becomes more thermally unstable or flammable over time, as suggested by historical accounts of nitrate film fires.

We established detailed testing protocols whereby the pristine film **CN-0** was aged under 25, 50, and 80 %RH at 60 °C in separate controlled environment chambers, while **CN-2** and **CN-4** were aged only under the most aggressive 80 %RH condition at 60 °C in environmental chambers. These accelerated aging conditions were selected in order to mimic storage environments ranging from a refrigerator to a humid film vault lacking careful humidity control. Prior to

accelerated aging, five contiguous film frames from each sample reel were cut, stacked, and fastened together using a Teflon-coated copper wire threaded through the sprocket holes located at the edges of the film. We intended for these film stacks to mimic the conditions of rolled film stored on reels within a film canister, within the limited space constraints of our accelerated aging apparatus. Each film stack was placed in a test tube of sufficient diameter (~ 2.6 cm) to avoid folding or rolling the film, and six film-loaded test tubes were placed in wide-mouth glass jars containing a seventh test tube filled with a specific saturated water/salt mixture to maintain the desired relative humidity condition within the container (see Figure 18). These sample containers were thermostatted at 60 ± 2 °C using an oven equipped with a PID temperature controller. A saturated $\text{MgCl}_2(aq)$ solution was used to maintain 30 %RH, saturated $\text{NaBr}(aq)$ for 50 %RH, and saturated $\text{KCl}(aq)$ for 80 %RH at 60 °C as measured using commercially available NIST-calibrated hygrometers at periodic intervals. We note that small variations in relative humidity were observed ($\pm 7\%$ from the target value). By removing sample stacks after 15, 30, 60, 90, 180, and 360 days of accelerating aging, we assessed how the physical and chemical state of the film changed as a function of time. Assuming that the degradation of our nitrate samples conforms to the previously reported Arrhenius kinetics, the 90-day time point in our 60 °C accelerated aging tests corresponds to ~ 13.8 years of aging in a 36 °F (2.2 °C) refrigerator. Under the same assumptions, 365 days of accelerated aging at 60 °C corresponds to 55.7 years of storage in a 36 °F refrigerator or 220 years in a 0 °F (-18 °C) freezer.

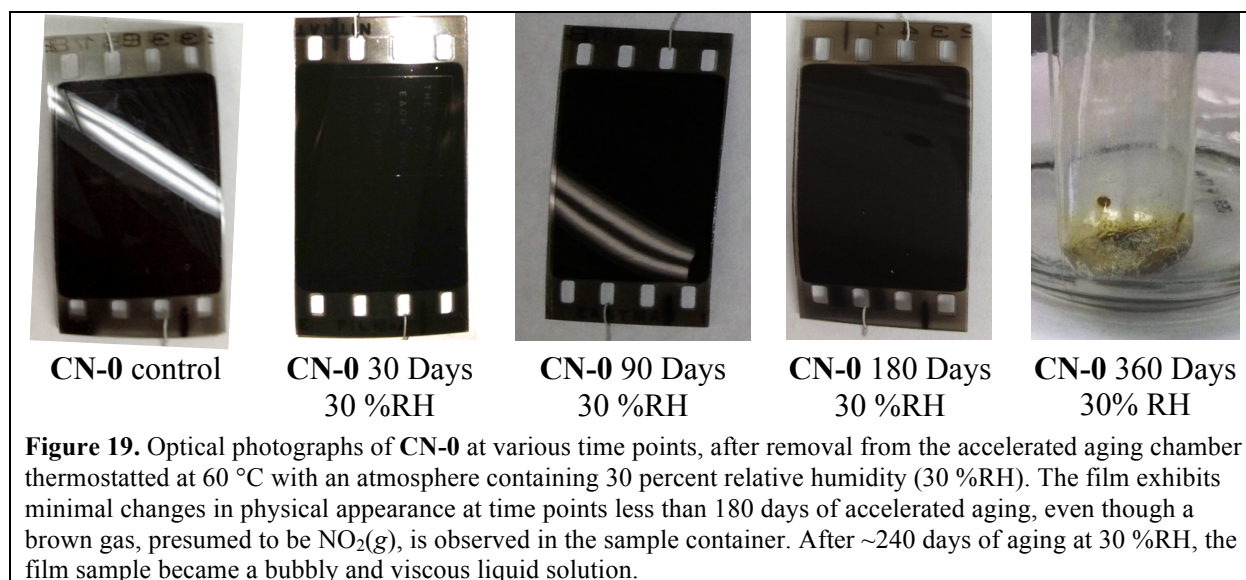


Figure 18. A wide-mouth glass jar with six film-loaded test-tubes and one test tube containing a water/salt solution to maintain the desired relative humidity, which was directly measured using a NIST-calibrated hygrometer.

In the following sections, we describe the results of our analyses of film samples subjected to these accelerated aging conditions under various relative humidities. After providing detailed findings for each sample aging condition in separate sections, we comparatively analyze the aggregate data to draw some conclusions from these experiments.

Accelerated Aging of CN-0 at 30 %RH:

Aging CN-0 at 60 °C under a 30 %RH atmosphere caused significant changes in the physical appearance of the film samples as documented in the photographs shown in Figure 19. We note that the physical appearance of the film was relatively unchanged after up to 90 days, and only a small amount of a brown gas is observed to build up in the sealed aging chamber over time. This brown gas is tentatively identified as $\text{NO}_2(g)$, arising from the denitration of the film. Film denitration generates nitric acid (HNO_3), which is in equilibrium with water and $\text{N}_2\text{O}_5(g)$ that may thermally decompose into $\text{NO}_2(g)$ and other nitrogen oxide byproducts. After 180 days of accelerated aging, the samples lose their sheen. Remarkably, the film degrades into a puddle of viscous, pale yellow liquid after ~ 240 days of aging. This decomposed product may be related to the “viscous froth” that appears on the surface of degraded nitrate film that falls under the Stage 4 classification.



Detailed analyses of the chemical constitution of the film reveal that this 30 %RH aging condition does not appear to cause the denitration of the film (Table 7). The IPI Acidity tests on samples removed at all of the time points indicate that the film pH ~ 5.5. Note that pH 5.5 is comparable to that of a control sample of water. (Note: the pH of water exposed to air is pH 5.5 due to the dissolution of CO₂(g) from the atmosphere.) ¹H NMR spectroscopy further demonstrates that the ratio of cellulose [dinitrate]:[trinitrate] remains nearly constant at ~1.2-1.3. These minor variations are within the error of the measurement and are thus considered statistically insignificant. These two chemical analyses suggest that the film remains largely intact until catastrophic degradation occurs at longer times.

Table 7. Results of Chemical and Physical Analysis of CN-0 Samples aged at 60 °C under 30 %RH

Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test ^a	5-5.5	4.5-5.0	5.5	5.5	5.5	6.0	4.0
¹ H NMR [(NO ₂) ₂]:[(NO ₂) ₃] ^b	1.23	1.227	1.21	1.28	1.25	1.303	<i>n.d.</i> ^d
Decomposition Onset Temp (°C) ^c	170.4±0.6	169.3±0.5	169.6±0.3	170.5±2.9	180.5±0.3	180.7±1.4	<i>n.d.</i> ^d
Deflagration Temp (°C) ^c	183.0±7.9	178.0±0.5	177.6±0.3	180.0±1.0	189.7±2.5	191.7±2.1	<i>n.d.</i> ^d

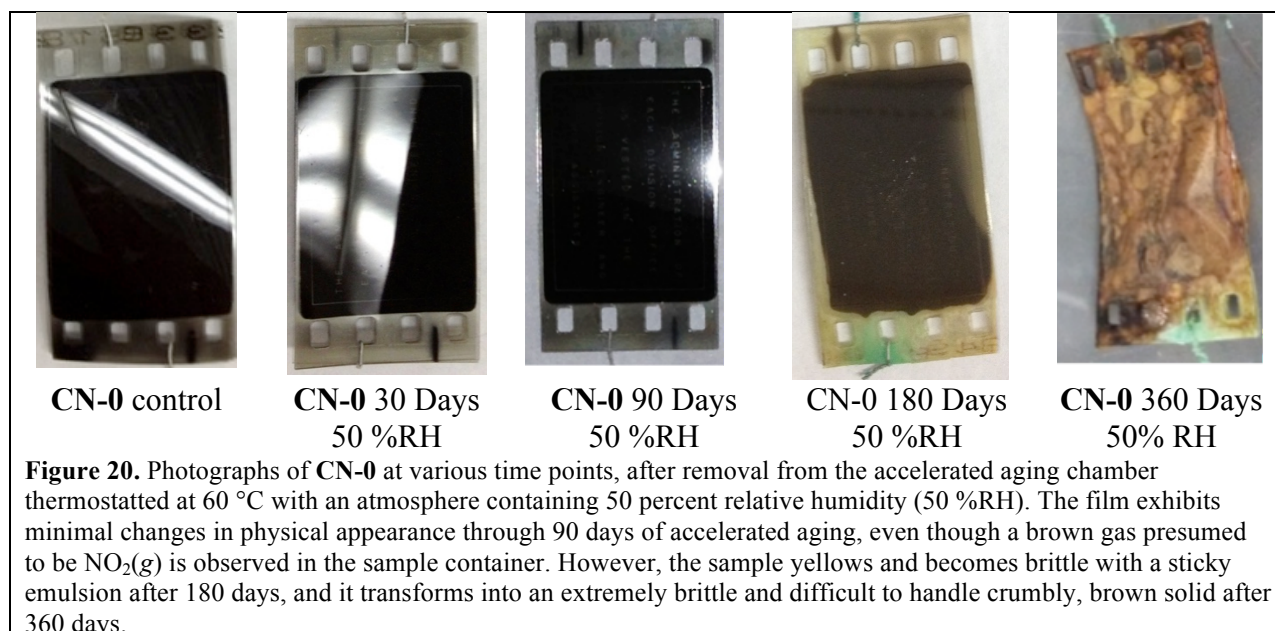
^a Determined by soaking 50 mg of film in 5 mL water at 22 °C for 24 h and subsequent pH measurement. ^b From quantitative ¹H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-*d*₆, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). ^c Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. ^d *n.d.* = not determined.

TGA analyses of CN-0 aged at 30 %RH demonstrate that the film samples exhibit similar thermal profiles to the initial CN-0 samples, with a slight decrease in combustibility after 90

days. Table 7 listed the decomposition onset temperature (T_{decomp}), at which the sample exhibits 5 % weight loss, and the deflagration temperature (T_{deflag}) for film bearing an emulsion layer. Both T_{decomp} and T_{deflag} remain near 170 and 180 °C, respectively, up to the 90 day time point. After 180 days of aging, these two temperatures increase by nearly 10 °C. However, we note that the shapes of the TGA profiles indicate that the samples initially bubble due to gas evolution and they subsequently deflagrate at a single temperature with nearly complete weight loss. In order to understand the effect of the gelatin (or emulsion) layer on flammability, we conducted TGA analyses on samples for which the gelatin layer had been removed by immersion in bleach and exhaustive washing with deionized H₂O. Removal of the gelatin layer did not change the observed values of T_{decomp} and T_{deflag} in a statistically significant manner.

TGA analysis could not be completed for the final 360 day sample that decomposed into a puddle of viscous liquid, but we conducted additional analyses aimed at identifying the molecular species present in the solution. ¹H NMR spectra of the liquid reveal a forest of sharp peaks, indicating complete degradation of the polymer into small molecule fragments. However, attempts to assign these peaks failed due to the density of peaks observed, likely arising from a complex array of nitrate film decomposition products. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) analyses of a sample in 10 mM CH₃COONH₄ in CH₃CN in positive ion detection mode showed that the mass-to-charge ratio (m/z) arising from the key molecular fragments observed in this analysis were m/z = 256, 270, 284, 360, 390, and 446 g/mol. The m/z = 270 fragment may correspond to a dinitroglucose arising from depolymerization of the cellulose nitrate film stock into its constituent monomers.

Accelerated Aging of CN-0 at 50 %RH:



Photographs of CN-0 aged under a 50 ± 5 %RH atmosphere at 60 °C display a different course of physical degradation, as shown in the photographs in Figure 20. In the first 90 days of the film aging, the samples physically appear unchanged and a significant amount of a brown gas is

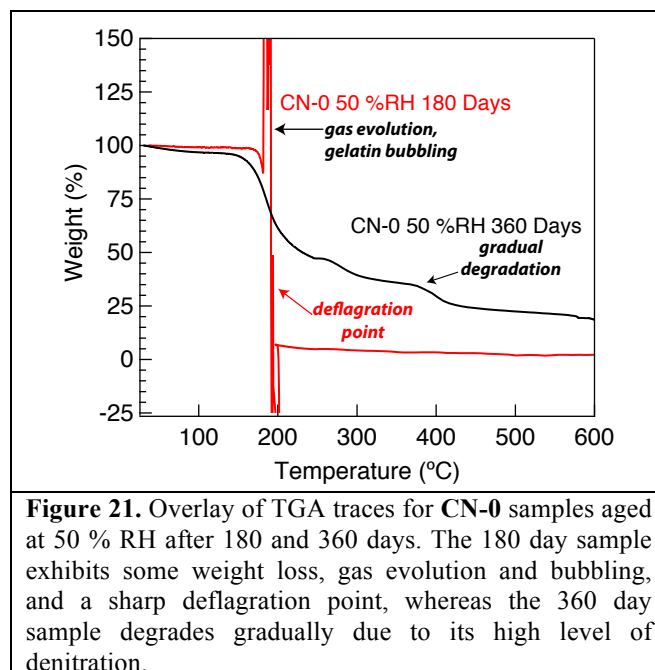
observed to accumulate in the sealed aging chamber. As previously mentioned, we surmise that this noxious brown gas is $\text{NO}_2(\text{g})$ arising from the thermal decomposition of nitric acid liberated from the film by hydrolysis. After 180 days, the film loses its sheen and the emulsion becomes uneven and sticky. At the final 360 day time point in this accelerated aging trial, we find that the film samples are extremely brittle, rusty brown solids. These final samples exhibit many of the physical attributes of deteriorated film stock that may ultimately decay into brown powder.

Table 8. Results of Chemical and Physical Analysis of CN-0 Samples aged at 60 °C under 50 %RH							
Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test ^a	5.0-5.5	4.5-5.0	5.5	5.5-6.0	5.5	3.5	2.5
¹ H NMR [(NO ₂) ₂]:[(NO ₂) ₃] ^b	1.23	1.237	1.257	1.287	1.27	1.817	7.177
<i>M_n</i> (kg/mol)	13.1	10.5	9.1	9.2	11.2	15.1	3.5
<i>D</i> = <i>M_w</i> / <i>M_n</i>	3.04	3.30	3.48	3.27	2.56	2.23	1.85
Decomposition Onset Temp (°C) ^c	170.4±0.6	170.3±0.5	168±1.0	170.6±1.2	180.4±0.9	181.1±0.4	156.2±8.0
Deflagration Temp (°C) ^c	179.4±0.5	178.5±0.3	179.2±0.5	187.5±1.0	189.7±4.8	193.1±2.4	gradual decomp. ^d
^a Determined by soaking 50 mg of film in 5 mL water at 38 °C for 24 h and subsequent pH measurement. ^b From quantitative ¹ H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone- <i>d</i> ₆ , by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). ^c Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. ^d No deflagration observed: gradual decomposition above 200 °C observed for both the native film and the bleached sample (gelatin removed).							

The results of both the IPI acidity test and ¹H NMR spectroscopic analyses of the film are consistent with the decay of these heritage nitrate samples by denitration (Table 8). The results of the IPI acidity test indicate that the film becomes significantly acidic after 180 days of accelerated aging with a measured pH = 3.5; it becomes even more acidic at 360 days (pH = 2.5). ¹H NMR spectroscopy shows that the ratio of cellulose [dinitrate]:[trinitrate] increases from a baseline value of 1.23 to 7.18 after 360 days of accelerated aging. Thus, the film appreciably denitrates as compared to the samples aged at 30 %RH. SEC analyses further indicate that the nitrate film base molecular weight is relatively invariant after 180 days of accelerated aging, and it precipitously drops as it denitrates.

The observed denitration of the film manifests in substantial changes in the thermogravimetric analyses of the samples aged at 50 %RH for varying amounts of time (Table 8). The decomposition onset temperature (*T*_{decomp}) initially increases from 170 °C to 181 °C between 0–180 days, and then it drops to 156 °C at 360 days. While this trend may seem counterintuitive, one must recognize that *T*_{decomp} measures only the temperature at which 5% weight loss is observed. The origin of the weight loss could vary. We speculate that as the film denitrates, it becomes more hydrophilic, and thus the 5 % weight loss temperature decreases as the film takes up water that is expelled at a lower temperature. (As noted in the differential vapor sorption studies above, highly nitrated cellulose CN-0 hardly takes up 3 wt% water at 50 %RH.) On the other hand, we observe that the deflagration temperature (*T*_{deflag}) increases monotonically with

time. The TGA profiles for the film aged for 180 days or less exhibit initial bubbling due to gas evolution, followed by catastrophic deflagration. However, the sample aged for 360 days exhibits a slower, staged degradation with signs of deflagration (see Figure 21). Thus, we observe that the film aged for 360 days at 50 %RH is not combustible.



Accelerated Aging of CN-0 at 80 %RH:

Aging CN-0 at 60 °C under an 80 %RH atmosphere results in the fastest degradation of the emulsion and yellowing of the nitrate film base layer as assessed by simple physical inspection (see Figure 22). After only 90 days under these conditions, the film emulsion is sticky and the base layer is yellow. These changes in the physical appearance of the film are accompanied by the formation of brown $\text{NO}_2(\text{g})$ in the aging chamber, which arises from HNO_3 decomposition. The gaseous product seems to react further with the gelatin layer. Thus, the film degrades from a Stage 0 pristine film to a Stage 2 material after only 90 days in our aging chamber. Degradation proceeds further to yield a liquid-like gelatin layer and a brown film base after 180 days of aging. Complete image degradation and embrittlement of the yellow-brown nitrate base layer occurs after 360 days.

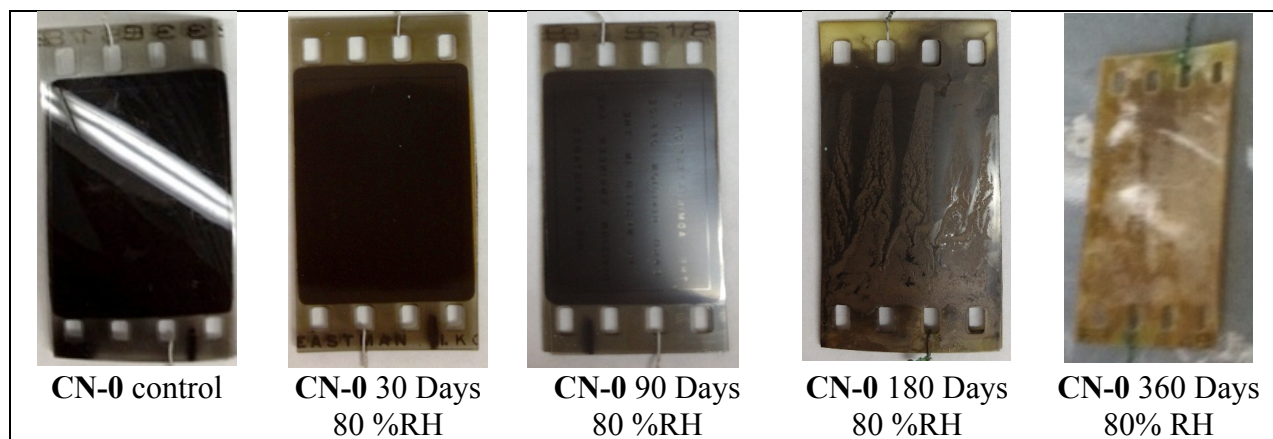


Figure 22. Pictures of CN-0 at various time points, after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 80 percent relative humidity (80 %RH). The film becomes sticky and slightly yellow in color after 90 days, whereas the film becomes brown with a liquid-like gelatin layer after 180 days. After 360 days, the emulsion is completely devoid of any image and the film base is brittle and yellow-brown in color. Note that gaseous $\text{NO}_2(\text{g})$ is observed in the sample container during the course of the aging trial.

IPI acidity testing suggests that the pH of the film drops to ~4.5 after 60 days of aging, and that the acidity generally hovers in the range pH = 4-5 throughout the aging trial (see Table 9). ^1H NMR analyses indicate that the film does denitrate to some extent, with the apparent ratio of cellulose [dinitrate]:[trinitrate] increasing from 1.23 to 1.4. Thus, the chemical composition of the film does not appear to appreciably change during aging at 80 %RH. The latter assertion is corroborated by the fact that the molecular weights of the film determined from SEC analyses were relatively invariant at all time points. These chemical findings are strikingly discordant with the results of the visual inspection of these aged samples at each time point, providing further evidence that the five-stage classification scheme for nitrate film degradation does not always accurately reflect the true chemical state of the film or its potential hazards.

Table 9. Results of Chemical and Physical Analysis of CN-0 Samples aged at 60 °C under 80 %RH

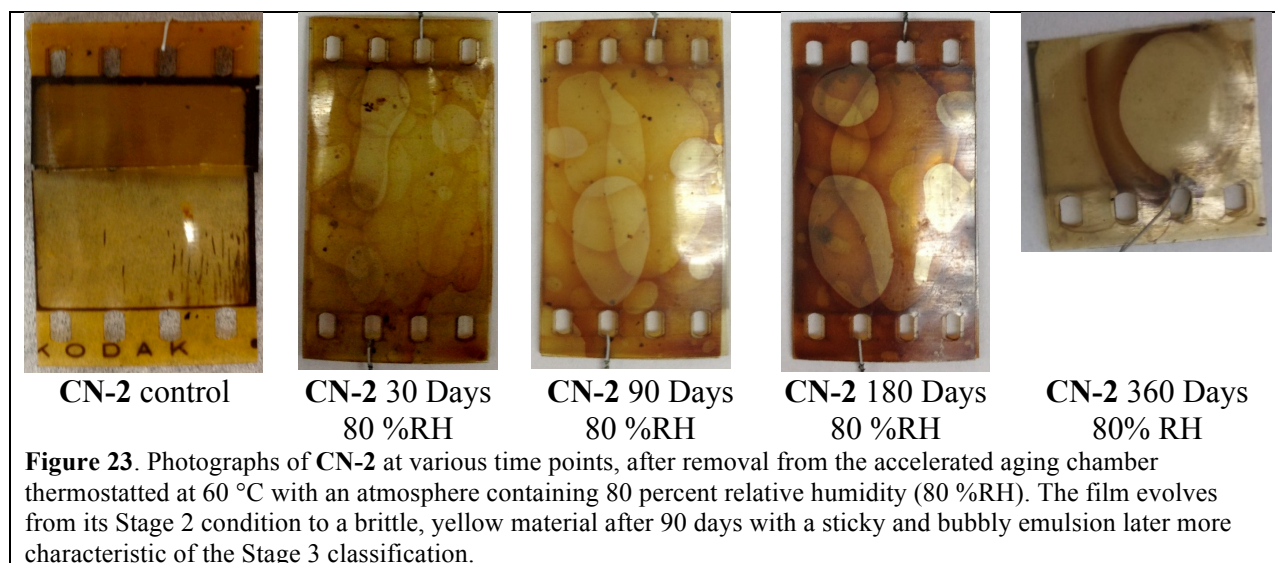
Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test ^a	5.0-5.5	5.0	5.5	4.5	5.0-5.5	4.0	5.0
^1H NMR [(NO ₂) ₂]:[(NO ₂) ₃] ^b	1.23	1.207	1.240	1.290	1.290	1.403	1.34
M_n (kg/mol)	13.2	9.7	14.4	13.1	14.2	12.5	14.4
$D = M_w/M_n$	3.04	3.57	2.65	2.39	2.41	2.39	1.96
Decomposition Onset Temp (°C) ^c	170.4±0.6	170.0±0.3	170.8±0.7	171.4±1.8	180.6±0.9	173.2±7.6	172.0±0.5
Deflagration Temp (°C) ^c	183.8±7.9	179.4±1.4	179.6±1.0	179.6±1.2	191.3±1.2	187.5±4.7	179.0±1.6

^a Determined by soaking 50 mg of film in 5 mL water at 22 °C for 24 h and subsequent pH measurement. ^b From quantitative ^1H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone- d_6 , by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). ^c Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C.

The relatively small changes in the chemical composition of the film described above are also consistent with the thermogravimetry results from these samples aged at 80 %RH (Table 9). The T_{decomp} and T_{deflag} values are relatively invariant with time, suggesting that the film flammability is least affected by the 80 %RH aging condition. Furthermore, TGA profiles for these samples indicate that the film forms bubbles due to gas evolution prior to nearly complete combustion. Thus, we conclude that the high relative humidity condition is the worst for image preservation and that the resulting product of decomposition retains its high flammability.

Accelerated Aging of CN-2:

In order to understand better how a partially degraded film sample decomposes, we also aged samples of **CN-2** under 80 %RH conditions for up to 360 days. This aging condition was selected by virtue of our initial intuition that higher relative humidity conditions would lead to greater levels of denitration and dramatic changes in the flammability profile of the film (*vide infra*). In Figure 23, one qualitatively observes the degradation of **CN-2** from Stage 2 to Stage 3, evidenced by the formation of islands and bubbles in the gelatin layer on top of the film base. This drastic change in the physical appearance of the film is accompanied by its acidification to



pH 3.5 after 60 days, as determined by the IPI Acidity Test (Table 10). We note that the acidity of the film recovers to some extent to pH 4.5 at longer times, possibly due to the equilibrium formation of gaseous nitrogen oxides due to thermolysis of HNO_3 . Since our sampling methodology involved opening the sealed container to extract samples at prescribed time points, the nitrogen oxides were allowed to escape from the container. By effectively removing the nitrogen oxides from the aging canister atmosphere, we may have artificially decreased the detected acidity of the film.

Table 10. Results of Chemical and Physical Analysis of CN-2 Samples aged at 60 °C under 80 %RH

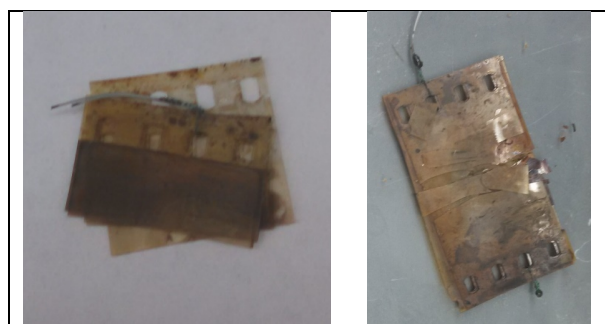
Time (days)	0	15	30	60	90	180	360
pH from IPI Acidity Test ^a	3.5-4.0	4.0	4.0	3.5	3.5-4.0	4.5	4.0-4.5
¹ H NMR ^b [(NO ₂) ₂]:[(NO ₂) ₃]	1.38	1.427	1.508	1.593	1.563	1.660	1.773
Decomposition Onset Temp (°C) ^c	161.1±0.8	157.1±0.9	156.4±0.6	160.0±0.3	160.8±0.3	161.3±1.7	166.7±0.5
Deflagration Temp (°C) ^c	179.9±0.3	gradual decomp	175.5±4.3	179.7±1.6	gradual decomp	182.1±1.2	186.7±0.4 ^d

^a Determined by soaking 50 mg of film in 5 mL water at 38 °C for 24 h and subsequent pH measurement. ^b From quantitative ¹H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-*d*₆, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). ^c Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. ^d The unbleached film deflagrates, whereas the bleached film (gelatin removed) exhibits only gradual decomposition at temperatures $T \geq 200$ °C.

TGA studies of the aged CN-2 film samples demonstrated wide variability in their deflagration behavior (Table 10). The decomposition onset temperature (T_{decomp}) was nearly invariant at ~160 °C at all time points in our study. However, the deflagration temperature (T_{deflag}) was nearly constant at ~180 °C, with the exceptions of the samples aged for either 15 and 90 days. The latter two samples do not deflagrate; instead, they exhibit gradual thermal decomposition profiles akin to that shown in Figure 12 for CN-0 aged under 50 %RH after 360 days. We are unsure of the

source of this variability in combustibility within this sample set. We initially suspected that the presence or absence of the gelatin layer and any metal salts arising from image decomposition could play a role in the flammability profile, yet the bleached film samples (gelatin removed) exhibited the invariant TGA profiles with the exception of the sample aged for 360 days.

Accelerated Aging of CN-4:



CN-4 control

**CN-4 360 Days
80% RH**

Figure 24. Photos of the initial CN-4 sample and after removal from the accelerated aging chamber thermostatted at 60 °C with an atmosphere containing 80 percent relative humidity (80 %RH) after 360 days. The film definitely becomes more brittle and discolored, although the changes in physical appearance are less dramatic than in the other samples subjected to accelerated aging.

Table 11. Results of Chemical and Physical Analysis of CN-4 Samples aged at 60 °C under 80 %RH

Time (days)	0	360
pH from IPI Acidity Test ^a	3.0–3.5	4.5
¹ H NMR [(NO ₂) ₂]:[(NO ₂) ₃] ^b	1.563	1.823
TGA		
Decomposition Onset Temp (°C) ^c	152.1±2.8	155.6±6.2
Deflagration Temp (°C) ^c	184.0±2.8	186.7±3.5

^a Determined by soaking 50 mg of film in 5 mL water at 38 °C for 24 h and subsequent pH measurement. ^b From quantitative ¹H NMR spectroscopy of bleached nitrate film stock (gelatin removed) in acetone-*d*₆, by comparative integration of the peaks at δ 5.76 ppm (cellulose 2,3,6-trinitrate) and δ 3.42 (cellulose 3,6-dinitrate). ^c Determined by TGA under oxygen (flow rate of 20 mL/min) using a ramp rate of 10 °C up to 200 °C followed by a jump to 600 °C. ^d Deflagration does not occur: the sample decomposes gradually with the first major weight loss occurring at a temperature T ≥ 200 °C.

As a corollary study to our CN-2 aging trials, we also aged one sample of CN-4 for 360 days at 80 %RH. We limited this analysis to a single data point after 360 days of accelerated aging, due to: (1) space limitations in our temperature-controlled chamber, and (2) the fact that CN-4 samples lack any intrinsic value due to the complete degradation of the image. Consequently, this analysis aimed only to understand the final stages of nitrate film decay. As with the aged CN-2 samples, aging CN-4 for 60 days at 80 %RH results in the film becoming more brittle and discolored (see Figure 24). Comparative ¹H NMR analyses of CN-4 prior to and after aging show that it does denitrate to some extent (see Table 11). However, the level of denitration is low, and thus the flammability profile of the samples assessed by TGA are nearly identical with deflagration occurring at ~187 °C. Thus, the film retains its flammability under the high relative humidity aging condition long after the image is degraded beyond use.

Cumulative Analysis of the Accelerated Aging Data:

Comparison of the data collected on all of the film samples subjected to accelerated aging trials under various relative humidity conditions at 60 °C provides some new insights into the deterioration behavior of cellulose nitrate film. At the lower relative humidity conditions (30 and 50 %RH), we observed that the emulsion layer remains intact up to ~90 days; the emulsion subsequently loses its sheen and takes on an uneven appearance. The 30 %RH sample unexpectedly depolymerized after ~240 days of aging into what we tentatively assign as an aqueous solution of partially nitrated glucose oligomers. However, the sample aged at 50 %RH

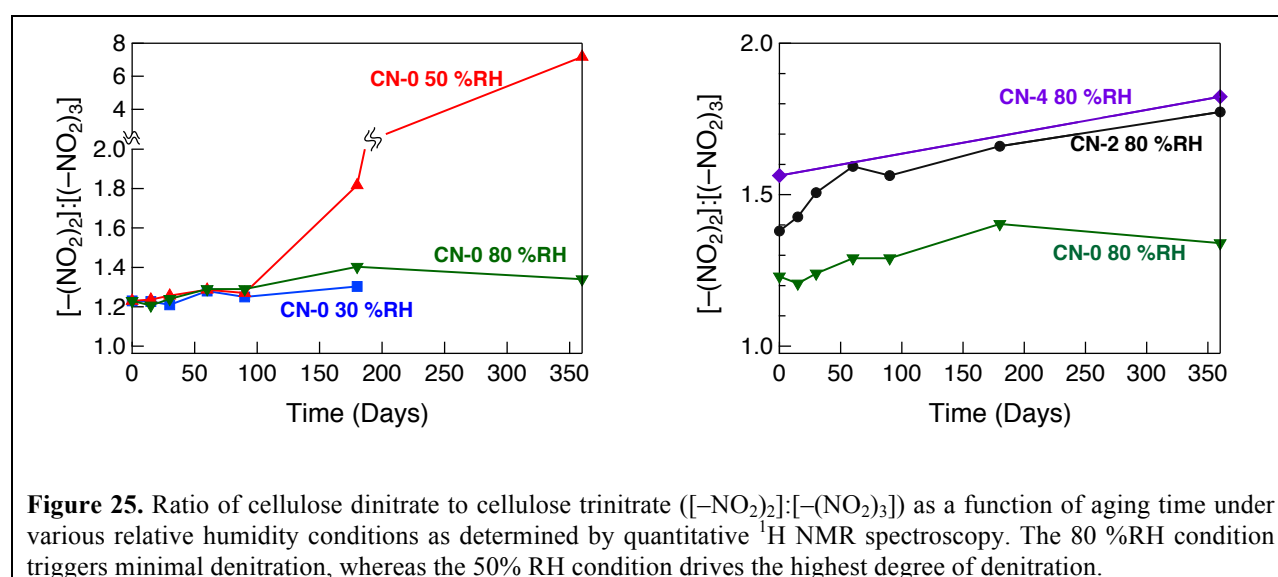
becomes a rusty brown solid that is extremely crumbly. We speculate that further aging of this sample might lead to the formation of “brown powder.” These results starkly contrast to those obtained for **CN-0** aged under an 80 %RH atmosphere, wherein the samples become sticky after 90 days, the emulsion becomes a sticky liquid after 180 days, and complete image degradation ensues by 360 days.

The aggregated ^1H NMR data for the **CN-0** samples aged under different RH conditions and the **CN-0**, **CN-2**, and **CN-4** samples aged at 80 %RH are presented in Figure 25. From these data, one clearly sees that: (1) the denitration of **CN-0** upon aging decreases in the following order

$$30\% \text{ RH} \sim 50\% \text{ RH} \gg 80\% \text{ RH},$$

(2) the 80 %RH condition leads to only low levels of denitration, even after 360 days of accelerated aging at 60 °C, and (3) IPI acidity tests of the film show that the pH decreases in the order

$$50\% \text{ RH} > 30\% \text{ RH} \gg 80\% \text{ RH}.$$



These results are somewhat surprising, as we initially expected that the denitration process would occur most quickly for the samples aged at the highest relative humidity condition. This expectation was based on the notion that water is required for the hydrolysis of the nitrate esters, which is the reverse process of the manufacturing process for nitrate film from cellulose: higher water concentrations should drive denitration. However, the data suggest that the 50 %RH condition drives denitration to the greatest extent and that the 30 %RH condition results in hydrolysis of both the nitrate esters and the backbone β -glucoside linkages to yield a syrupy solution. SEC data further demonstrate that the molecular weight of the film base is relatively unchanged at the highest relative humidity condition, yet the molecular weight drops upon aging at lower relative humidities (see Figure 26).

The chemical composition of the aged nitrate film samples is strongly correlated with the corresponding thermogravimetric analysis profiles, with higher levels of nitration implying lower deflagration temperatures. These data are plotted in Figure 27. The decomposition onset temperature (T_{decomp}) is relatively invariant for the **CN-0** aged under different relative humidity atmospheres. While this observation may seem surprising, it is important to remember that the decomposition onset temperature reflects the temperature at which the film sample has lost 5 % of its initial mass during heating at 10 °C/min from 22 °C. Slight decreases in T_{decomp} may arise from denitration of the film that increases its water uptake, so that the mass loss at temperatures $T \leq T_{\text{decomp}}$ originates from water evaporation. Except for the **CN-0** aged under 30 %RH or 50 %RH that significantly denitrate, all of the other film samples have deflagration temperatures (T_{deflag}) in the range ~170–180 °C that are consistent with their low levels of denitration. The 50 %RH **CN-0** sample aged for 360 days does not deflagrate and instead decomposes gradually as shown in the TGA profile Figure 18.

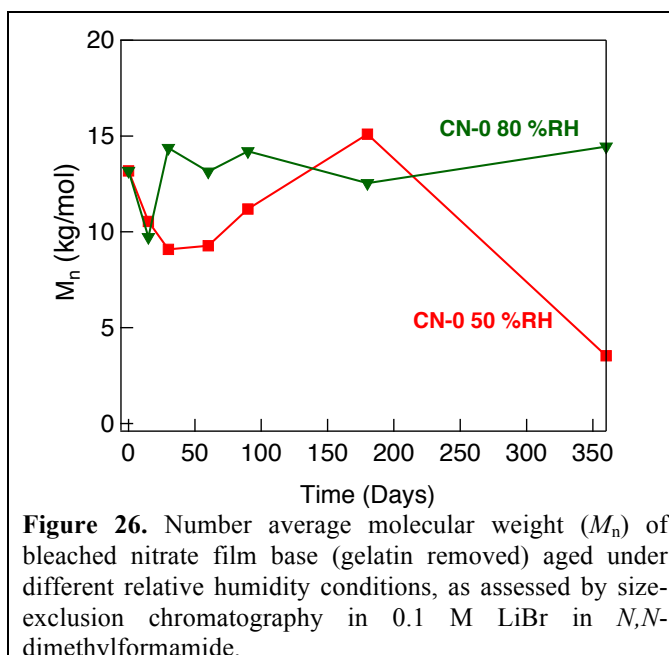


Figure 26. Number average molecular weight (M_n) of bleached nitrate film base (gelatin removed) aged under different relative humidity conditions, as assessed by size-exclusion chromatography in 0.1 M LiBr in *N,N*-dimethylformamide.

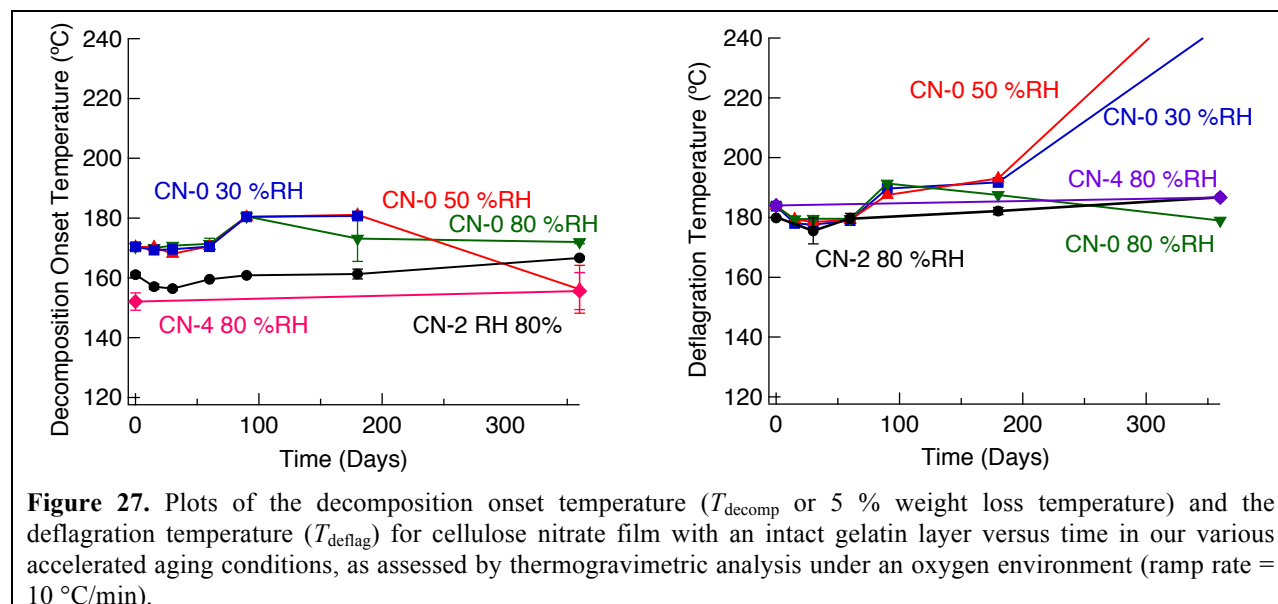


Figure 27. Plots of the decomposition onset temperature (T_{decomp} or 5 % weight loss temperature) and the deflagration temperature (T_{deflag}) for cellulose nitrate film with an intact gelatin layer versus time in our various accelerated aging conditions, as assessed by thermogravimetric analysis under an oxygen environment (ramp rate = 10 °C/min).

While the observed trend of high levels of film denitration at lower relative humidity aging conditions seems counterintuitive, a simple chemical model accounts for our observations. To understand acid-catalyzed degradation of nitrate film, one must consider the underlying thermodynamics of nitrate ester hydrolysis and the kinetics (or rate) of hydrolysis. From a thermodynamic viewpoint, water is a necessary ingredient for the hydrolysis reaction, and the

presence of increasing amounts of water (e.g., higher relative humidities) increases the thermodynamic driving force for the hydrolysis reaction. However, thermodynamics only assesses reaction feasibility—not the rate at which it occurs. The rate of the hydrolysis reaction depends on the concentrations of the reactants—specifically, the concentration of nitrate esters, nitric acid, and water. Since the reaction is heterogeneous (one in which the reactants are present in more than one phase, including gases, liquids, and solids), one must formally write the reaction rate as a product of the activities of each species. The activities of each species reflect the “effective active amount” of each reactant in the mixture, which may deviate either positively or negatively from the actual reagent concentration. Thus, the hydrolysis of nitrate film depends sensitively on the activities of both water and the nitric acid (HNO_3) catalyst. Sasahira *et al.* studied the activities of water (a_{water}) and nitric acid (a_{HNO_3}) in nitric acid solutions (*J. Nucl. Sci. Technol.–T.*, **1994**, 31, 321–328). Based on the data reported therein, we calculated the product of the activities $a_{\text{water}} * a_{\text{HNO}_3}$ for a variety of [water]:[nitric acid] ratios. We find that this product of activities reaches a maximum at a mole fraction $x_{\text{HNO}_3} = 0.42$ and $x_{\text{water}} = 0.58$. In other words, the rate of the hydrolysis reaction is expected to peak at some intermediate relative humidity.

This detailed chemical picture may also be understood in more qualitative terms. At low relative humidity, the HNO_3 present in the film is poorly hydrated and thus its effective active concentration is relatively low. We speculate that the small amount of water present competes with the cellulose backbone oxygens to preferentially solvate the acidic protons. Thus, the backbone β -glucoside linkages cleave to depolymerize the film base into nitroglucose oligomers. At intermediate relative humidities, the effective active concentration of acid increases due to the better solvation of the HNO_3 by the larger amount of water. This improved solvation of the HNO_3 leads to acid dissociation to form H_3O^+ which catalyzes nitrate ester hydrolysis. At very high relative humidities, the dissolved H_3O^+ ions become so stable that they are unavailable to participate in the hydrolysis of either the β -glucoside backbone linkages or the nitrate esters. Hence, hydrolysis is fastest at intermediate water concentrations and intermediate relative humidities.

We found that the 50 %RH humidity accelerated aging condition initially enables maintenance of the film image carried by the emulsion layer, followed by decomposition of the nitrate stock into a non-hazardous solid.

5. Assessing the Hazards of “Brown Powder” Arising from Nitrate Film Decomposition

The potentially hazardous nature of the “brown powder” arising from the nearly complete decay of cellulose nitrate film (Stage 5 of the decomposition model) is the source of substantial anxiety in the film archivist community. Literature and anecdotes about the powder stage of nitrate are particularly contradictory; some—such as the International Standard *ISO 10356*—maintain that the powder is comparable to the flammability of paper, while others—such as Kodak’s legal *Material Safety Data Sheet*—claim that it is “shock sensitive,” like gunpowder or nitroglycerine. Additional research has also suggested that the powder might be formed by a reaction between the cellulose nitrate base and metal storage cans, further complicating our understanding of the powder’s relationship to nitrate film’s decomposition. We therefore sought to quantitatively evaluate the shock and friction sensitivity of brown powder by direct mechanical analysis, as a complete understanding of its controversial properties significantly affects how curators of

nitrate collections handle and dispose of film stocks that have degraded beyond any useful condition.

By soliciting various sources (who wish to remain anonymous), we obtained four samples of brown powder from two geographically diverse major film archives, hereafter referred to as “Archive 1” and “Archive 2.” The provenance and other characteristics of these brown powder samples are provided in Table 12. These samples were specifically chosen due their variable provenance and to the fact that the shock and friction sensitivity tests required a minimum of five (5) grams of brown powder.

Table 12. Characteristics of Acquired Brown Powder Samples

Sample Name	Archive	Sample Mass (g)	Film Stock
A1-1	1	5	unknown
A1-2	2	30	1929, no manufacturer markings
A1-3	2	30	1937, probably KODAK stock
A2-1	2	5	unknown

We sought to test the shock sensitivity of these four brown powder samples using a well-established standard, which could potentially inform the community of nitrate archivists of how best to handle and transport brown powder samples. The 2009 *United Nations Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria* (5th edition, 2009; <https://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev5/English/ST-SG-AC10-11-Rev5-EN.pdf>, accessed on Dec. 1, 2015) describes a battery of tests for determining the sensitivity of potentially dangerous materials to a variety of conditions to which they may be subjected during shipment. Section 13.4.2 therein provides a detailed description of the BAM Fallhammer test as one means of quantifying the shock sensitivity of a solid substance. Summarily, this test involves impacting a solid sample (~ 40 mm³) with weights of precisely known mass that are dropped from a precisely measured height. The test is typically conducted at least five times to ensure reproducibility. Since the potential energy of the mass in its initial condition is completely converted into kinetic energy imparted to the sample upon impact, one can determine the minimum amount of energy (measured in Joules (J)) required for the impact to cause a flash, flame, or explosion. U.N. recommendations state that materials with a limiting impact energy of ≥ 2 J are too shock sensitive to transport.

Chilworth Technology Inc. is a commercial safety and compliance analysis company that routinely conducts BAM Fallhammer tests using an apparatus developed by the Bundesanstalt für Materialforschung und Materialprüfung (BAM or German Federal Institute for Materials Research and Testing, located in Berlin, Germany). We sent samples of each of the brown powder samples to Chilworth for testing. For all four samples, the BAM Fallhammer test demonstrated that the required energy for flame, flash, or explosion was > 60 J, with no change in the sample appearance when compared before and after testing. Their analyses demonstrated that the samples were “not particularly sensitive to ignition by mechanical impact.”

The BAM Friction Test is another metric by which the *U.N. Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria* document advised testing the friction sensitivity of a material. Described in Section 13.5.1 therein, the BAM Friction Test involves dragging a porcelain peg of a precisely known mass over a sample of the test material on a porcelain plate at a constant rate. Since the mass of the porcelain peg is known, the friction force

(measured in Newtons (N)) exerted upon the material may be calculated. The threshold mass and thus the threshold value of the friction required for flame, flash, or explosion is measured. This test is conducted at least six times to ensure reproducibility of the results. For reference, the UN Manual listed the limiting friction load for dry nitrocellulose (13.4 wt% nitrogen) as 240 N, and the relatively stable explosive TNT has a threshold friction value of 360 N. According to tests conducted by Chilworth Technology Inc., the limiting friction load associated with all four of the brown powder samples was > 360 N. According to Chilworth's analytical team, these results indicate that these samples are "not sensitive to ignition by friction."

Therefore, our studies suggest that the samples of brown powder solicited from geographically distinct sources and variable provenances were non-hazardous solids. This result is consistent with qualitative shock sensitivity tests conducted by a member of the chemistry research team, using a standard tool hammer to impact samples of a fifth brown powder sample of unknown provenance. Attempts to analyze the composition of the latter brown powder sample by ^1H NMR spectroscopy were hampered by its poor solubility in hot deuterated water (D_2O) and $\text{DMSO}-d_6$. The fraction of the solid soluble in $\text{DMSO}-d_6$ exhibits a spectrum comparable to that of a significantly denitrated cellulose nitrate film stock. Against the caveat that we have tested a limited number of brown powder samples with only partially known provenance, we conclude that brown powder is non-hazardous on the basis of our dataset.

The official reports from Chilworth Global are included in Appendix 4.

Additional Initiatives

Annotated Bibliography

A major task of the history group was the creation of an annotated bibliography. Principally managed by Amanda McQueen, the bibliography was designed to be a relatively comprehensive, cross-disciplinary collection of literature on cellulose nitrate. Starting with the preliminary bibliography compiled by Heather Heckman and submitted in the grant application, we gathered sources from a variety of communities: archivists and conservators, chemists and polymer scientists, historians, film industry practitioners, safety or standards organizations, and government agencies. As a result, the bibliography contains a diverse set of sources, including: peer-reviewed, trade and popular press articles; historical accounts; literature reviews; websites and forum postings; conference proceedings; practitioner handbooks; safety standards; and government publications.

As we collected these sources, we organized them using the citation manager software EndNote. Each bibliographic entry was classified by type and by the community from which it originated, and each was furnished with an abstract, an annotation, and relevant keyword tags. The abstract is a neutral summary of the source's content. When possible, the abstract was taken from the source itself; otherwise, it was written by one of the graduate student researchers working on the project. The annotation, on the other hand, describes how relevant each source is to the overall goal of the grant project and points out any particularly noteworthy elements of its content. Finally, the history, conservation, and chemistry groups, drawing from the larger goals and research questions of the project, developed an extensive list of possible keywords covering a

wide range of topics, including: type of cellulose nitrate (e.g. motion picture film, sheet film, lacquer or adhesive), nitration level, plasticizers, film processing and handling, historical film fires, parameters of chemical studies, analytical techniques, mechanisms for decomposition, variables affecting decomposition and flammability, brown powder, and public relations. Each entry was then tagged with as many of these keywords as was applicable (A full list of keywords is available in Appendix 5). Not only do the tags allow someone viewing the bibliography to quickly ascertain which topics a given entry covers, they also facilitate more advanced sorting and organizing, as sources that cover similar material can readily be grouped together.

The annotated bibliography was meant to help all members of the grant project develop a stronger historical background that could inform our chemical research. However, it is also intended to be a useful resource for the broader public. By bringing together literature from a variety of disciplines, we have created a repository of information that can guide future scientific study and facilitate future conversation between the different communities that handle and study cellulose nitrate.

At this time, the bibliography contains 228 annotated sources, and a searchable and sortable version of the full annotated bibliography will be available on the Nitrate Website (discussed below). Four sample annotated bibliography entries are provided in Appendix 5.

Oral History Project

In August 2014, the history and conservation groups began work on an oral history project. By recording the anecdotal experiences of veteran professionals who have worked with nitrate film in a variety of capacities, we hoped to make sense of some of the lore surrounding this material and give voice to particular forms of knowledge that would be of interest and use to our intended audience. A list of experts was selected from four fields—archivists, conservators, laboratory personnel, and projectionists—that we believed would provide us with edifying accounts of their experiences. These colleagues were: Ken Weissman, Supervisor of the Film Preservation Laboratory for the Library of Congress' Packard Campus for Audio Visual Preservation; Paul Spehr, former Secretary for the Motion Picture Section of the Library of Congress and Assistant Chief of the Motion Picture Broadcasting and Recorded Sound Division of the Library of Congress; Rosa Gaiarsa, Collections Services Manager for the UCLA Film and Television Archive; Jess Daily, former Chief Projectionist at the UCLA Film and Television Archive; and Janice Allen, owner and manager of Cinema Arts film laboratory.

Each of these professionals was asked to share their knowledge in a recorded interview. Given that the interviewer would need to have some knowledge of nitrate in order to guide the questions appropriately, we decided that members of the conservation group would develop the interview format and conduct the phone interviews. In each case, the interview followed a set of questions that were tailored to the interviewee's field, whether archiving, film projection, or film lab experience (see Appendix 5). The interviews were designed to take an hour or less, and each was conducted by phone in the summer of 2015. Each will be streamed on the Nitrate Website, accompanied by written transcripts, a sample of which is included in Appendix 5.

Website

One of the chief methods of disseminating our findings will be via the Nitrate Website, which is hosted through the website for the Wisconsin Center for Film and Theater Research. All members of the history and conservation groups are contributing to the Nitrate Website, and the web design is being done by Michael Trevis, Instructional Specialist in the Department of Communication Arts. Covering all the major components of the grant project—its origins and research goals, the physicochemical analysis, the annotated bibliography, the survey, and the oral history—the website is designed to present our research and preliminary findings to a wider audience.

In particular, we aim to translate our chemical research into language that will be accessible to film archivists, conservators, and historians, many of whom may not have a strong scientific background. To assist in this endeavor, we created several short videos—ranging from 30 seconds to just under 2 minutes in length—that will work in conjunction with the website's prose to clarify and to visualize how these tests were performed. Videos were created for the following tests: thermogravimetric analysis (TGA), gel permeation chromatography (GPC), proton nuclear magnetic resonance (^1H NMR), and the accelerated aging trial. Each video shows Milton H. Repollet-Pedrosa, one of the chemistry graduate research assistants, performing a given analysis, and the videos for accelerated aging and TGA also contain a voice over explanation (the others are silent). A fifth video shows Amanda McQueen, the graduate student research assistant for the history and conservation groups, performing and explaining the steps of the physical inspection process. These videos were shot and edited by F. Booth Wilson, a Ph.D. candidate in the Department of Communication Arts, with assistance from Amanda McQueen. Input and feedback on the videos was provided by members of the history and conservation groups.

The website also provides access to the complete annotated bibliography. Users will be able to filter the bibliography entries based on type of publication—book, journal article, etc.—or by keyword. The keywords will be presented in a dropdown menu, and will consist of an abridged list of the keywords used in the annotations. This feature, in particular, will allow users to find articles related to more specific areas of interest, such as those that talk about nitrate film fires or those that contain chemical studies.

Finally, the website will include the full survey results, and the interviews conducted for the oral history project. For the latter, users will have access to both streaming audio files and written transcripts of the interviews.

We expect the website to go live in the coming months.

Regulatory Agencies

Our efforts to effect regulatory change were directed chiefly at the National Fire Protection Association (NFPA) and at NFPA 40, the Standard for the Storage and Handling of Cellulose Nitrate Film.

In response to the findings of our survey of archival professionals, described above, which demonstrated the disparities between the members of the Association of Moving Image Archivists (AMIA) and the members of the Council of State Archives (CoSA) in terms of level of knowledge and day-to-day practices governing nitrate storage and handling, these two organizations—working with members of the Wisconsin Nitrate Film Project—separately proposed first drafts of revisions for the forthcoming version of NFPA 40 (2016). NFPA then proposed the formation of a task group comprised of community members, members of NFPA that work with NFPA 40, and outside archivists to work on proposals for a second draft of revisions. Ultimately, most of the proposed changes were rejected, but NFPA has changed the review cycle for NFPA 40 and has reconvened the NFPA 40 task group, which includes two members of this research group. It may be possible, therefore, to revisit this issue in the future, as discussed in the conclusion of this report.

It was discovered during this process that there are a few gaps that complicate changing NFPA 40. First, there is an art to writing “actionable code”; the proposed changes must be put in the correct language for the NFPA committee. Quite often, this is done by professionals that specialize in such language. Second, more involvement from archivists and conservators is needed. Those who understand the needs and nuances of archival practice and can represent that community to NFPA need to become part of the revision process by submitting proposals for revisions, becoming members of the special archival task force, and attending meetings.

In the summer of 2015, Mahesh Mahanthappa and Katie Mullen also investigated the option of creating our own Material Safety Data Sheet (MSDS) for cellulose nitrate film. On the recommendation of Tilak Chandra, Senior Environmental Health Specialist at the University of Wisconsin–Madison, Mullen approached Dr. Neal Langerman, of Advanced Chemical Safety Inc., who explained the steps required and who advised against it. As the University of Wisconsin and the Wisconsin State Historical Society are not producers of nitrate, Langerman believed that the legal responsibilities these institutions would incur in the process of producing an MSDS would expose them to significant liabilities. However, he did suggest some alternatives: working with Kodak to amend their MSDS in light of our findings about brown powder, and writing a Standard Operating Procedure (SOP) for nitrate materials that would be used on the UW-Madison campus. Both of these options are discussed more below.

Continuation of Project, Avenues for Future Research, and Advocacy

Going forward, a number of scientific questions remain. First, there is the question of provenance. We recognize that our chemical tests and accelerated aging trials utilized a limited sample set. Indeed, the availability of samples is one of the chief difficulties of performing such studies. Future work on nitrate, then, might conduct the same tests we performed on a wider array of cellulose nitrate film stock samples, in order to assess and to establish the generality of our findings. Such studies would either validate our own findings, or, conversely, would point out anomalies therein that could direct future research. The question of storage cans also remains. One of our initial research questions concerned the role played by metal cans in the decomposition process, as a previous study by Edge (*Eur. Polym. J.*, **1990**, 26, 623-630) suggested that iron ions derived from film canister decomposition could accelerate the catalytic decomposition of nitrate film stock. While we were not able to incorporate this potentially

important variable into our own study, it might prove to be a useful avenue of future research, particularly given the restrictions governing the storage of nitrate in extant regulatory literature.

In addition, future research on cellulose nitrate should include sheet film. Far more archives hold heritage nitrate sheet film than nitrate motion picture film, yet various regulations which govern nitrate film are poorly adapted to the storage and handling of nitrate sheet film, and the institutions who hold it are less engaged with and aware of the regulatory process. Members of the National Fire Protection Association (NFPA) Committee on Hazardous Chemicals, which reviews proposed changes to NFPA 40, the Standard for the Storage and Handling of Cellulose Nitrate Film, suggested to Katie Mullen during the second draft revision meeting that specific data from chemical testing of heritage nitrate sheet film would enable the drafting of informed language allowing changes in the storage and handling of these collections. Studies focused just on sheet film or studies that are built around a comparison of sheet film and reel film would thus be of tremendous interest and practical utility to the archival and conservation communities.

Furthermore, there are still steps to be taken on the regulatory front. The special archival task force of the NFPA will continue, and NFPA would welcome more members from the archival community to this task force. Information about how to propose revisions to NFPA 40 can be found on the NFPA website, and any member of the public is able to submit proposals. Our survey demonstrated that the archival community lacks sufficient resources to meet all the regulatory requirements, and many institutions still have questions regarding the best preservation practices. The community must decide how to balance their preservation needs with regulatory restrictions and determine how to further engage with organizations like NFPA.

Two additional options for seeking regulatory change were suggested by Dr. Neal Langerman, of Advanced Chemical Safety Inc., in the summer of 2015. He proposed first that we approach Eastman Kodak Company and ask them to harmonize their Material Safety Data Sheet (MSDS) on nitrate film with our findings from Chilworth Global. While Kodak's MSDS claims that the brown powder is shock sensitive, our data from Chilworth demonstrates that it is inert. However, as Kodak is no longer a film manufacturer, they are under no obligation to produce a new MSDS. Additionally, the company's bankruptcy will likely further complicate communications with them. Langerman further suggested that we could work with Tilak Chandra, Senior Environmental Health Specialist at the University of Wisconsin–Madison, to create a Standard Operating Procedure (SOP) for the handling of cellulose nitrate film on the University of Wisconsin–Madison campus. Our findings about the brown powder could be published as an appendix to that document. We could then take our SOP to the International Standards Organization committee that deals with the handling and storage of nitrate film.

Finally, we are working to determine the best ways to translate our findings into pragmatic practices for archivists and conservators. Upon peer review of our chemical research, we will be in a better position to suggest practical applications of our findings to improve safety in archival practices. While the visual analysis methods we investigated did not yield consistent results, it is perhaps worth continuing to investigate whether there are simple tools which archivists could use to discern correlations between physical appearance and the chemical condition of heritage nitrate film. Furthermore, while our relative humidity findings cannot be directly translated into storage conditions for many reasons, the archival community would benefit from further

investigation of our findings. Our findings may serve as a long-term basis for future work by archivist and conservators with the NFPA to implement regulatory changes. While the timescale of such changes may seem long, the knowledge gained through this study may aid in the continued preservation of our nitrate film heritage with an emphasis on safety.

Appendix 1: Survey of Archival Practices

1. Survey questions sent to AMIA and CoSA
2. Survey respondents, with identities redacted
3. Full report of survey results

Wisconsin Nitrate Film Project Survey: AMIA

Q1 Please provide the following information: (Answers will remain confidential)

Your name and the name of the institution with which you are affiliated (if applicable)

Is your institution public or private?

How many employees are at your institution and/or what is your institution's operating budget?

Q2 Approximately how many reels of film comprise your entire collection?

Q2a How many reels of nitrate film do you hold?

- ☐ Enter Number of Reels _____
- ☐ None

Q3 Is your film collection housed in a specially constructed storage facility?

- ☐ Yes
- ☐ No

Q3a Which of the following best describes the storage for your film collection?

- ☐ Household freezer
- ☐ Commercial walk-in freezer
- ☐ Chemical freezer
- ☐ NFPA 40-compliant vault
- ☐ Vented room (please describe) _____
- ☐ Other (please describe) _____

Q3b Is nitrate film segregated from other materials?

- ☐ Yes
- ☐ No

Q4 How often do you inspect your nitrate holdings?

- ☐ Never
- ☐ Every 3 months
- ☐ Every 6 months
- ☐ Every 9 months
- ☐ Annually

Q4a If you have an established procedure for inspecting your nitrate, please describe it briefly.

Q5 In your handling of nitrate, do you consult and are you influenced by the guidelines for any of the following regulatory organizations (please select all that apply):

- ☐ NFPA 40 (storage and playback)
- ☐ OSHA (employee health/respiratory safety, mandated training)
- ☐ IATA & DOT (shipping)
- ☐ EPA (disposal)
- ☐ International / Non-American organizations

Q6 Please rank the following in terms of what you understand to be the most important conditions for minimizing risk and maximizing preservation for nitrate film:

- _____ Temperature control
- _____ Relative humidity control
- _____ Use of vented cans
- _____ Dedicated vault storage
- _____ Proper projection & handling

Q6a Which of the following categories for minimizing risk and maximizing the preservation of nitrate film is your facility able to meet? (please select all that apply)

- ☐ Temperature control
- ☐ Relative humidity control
- ☐ Use of vented cans
- ☐ Dedicated vault storage
- ☐ Proper projection & handling
- ☐ None

Q7 Do you have the occasion to transport nitrate film?

- ☐ Yes
- ☐ No

Q7a Have you been trained in the packaging and shipping of nitrate?

- ☐ Yes
- ☐ No

Q7b What has prevented you from receiving training and certification? (please select all that apply)

- ☐ Money
- ☐ Time
- ☐ Availability
- ☐ Lack of institutional support
- ☐ Other _____

Q8 Has the perception of nitrate film as dangerous or the difficulty of dealing with regulations caused you to not accept or deaccession nitrate film in good condition?

- ☐ Yes
- ☐ No

Q9 How have you learned about nitrate? (please check all that apply)

- ☐ University-level education or training
- ☐ On-the-Job training
- ☐ Workshops
- ☐ Conferences
- ☐ Books or articles
- ☐ Listserv discussions
- ☐ Casual conversation with others

Q9a

	Not confident at all (1)	A little confident (2)	Somewhat confident (3)	Confident (4)	Very confident (5)
How confident do you feel about your knowledge of nitrate?	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>

Q10 Have you had any direct experience with nitrate fires?

- ☐ Yes
- ☐ No

Q10a Please briefly describe your experience with nitrate fires.

Q11 Have any nitrate films in your collection noticeably deteriorated over time?

- ☐ Yes
- ☐ No

Q11a What steps did you take upon noticing the deterioration of nitrate?

Q11b To what do you attribute the lack of noticeable deterioration of your nitrate collection?

Q13 What kind of knowledge would be most useful to convert into practice? What information would be helpful to you in your storage and handling of nitrate? (Optional)

Wisconsin Nitrate Film Project Survey: CoSA

Q1 Your name and the name of the institution with which you are affiliated.

Q2 Total number of current employees who have as all or part of their responsibility nitrate film in all formats (flat, moving image, photo)

Q3 How many estimated number of reels of nitrate motion picture film do you hold?

- ☐ Enter Number of Reels _____
- ☐ None

Q4 How many estimated cubic feet or number of nitrate flat/still/sheet negatives do you own?

- ☐ Enter Number of Cubic Feet _____
- ☐ None

Q5 Is your film collection housed in a specially constructed storage facility?

- ☐ Yes
- ☐ No

Q6 Which of the following best describes the storage for your film collection?

- ☐ Household freezer
- ☐ Commercial freezer
- ☐ Commercial walk-in freezer
- ☐ Chemical Freezer
- ☐ NFPA 40-compliant vault
- ☐ NFPA 40-compliant cabinet
- ☐ Vented room (please describe) _____
- ☐ Other (please specify) _____

Q7 Is nitrate film segregated from other materials?

- ☐ Yes
- ☐ No

Q8 How often do you physically inspect your nitrate holdings?

- ☐ Never
- ☐ Every 3 months
- ☐ Every 6 months
- ☐ Every 9 months
- ☐ Annually

Q9 If you have an established procedure for inspecting your nitrate, please describe it briefly.

Q10 In your handling of nitrate, do you consult and are you influenced by the guidelines for any of the following regulatory organizations (please select all that apply):

- ☐ NFPA 40 (storage and playback)
- ☐ OSHA (employee health/respiratory safety, mandated training)
- ☐ IATA & DOT (shipping)
- ☐ EPA (disposal)
- ☐ International / Non-American organizations

Q11 Please rank on a scale of 1-5 the following in terms of what you understand to be the most important conditions for minimizing risk and maximizing preservation for nitrate film:

- _____ Temperature control
- _____ Relative humidity control
- _____ Use of vented cans
- _____ Dedicated vault storage
- _____ Proper projection & handling

Q12 Which of the following categories for minimizing risk and maximizing the preservation of nitrate film is your facility able to meet? (please select all that apply)

- ☐ Temperature control
- ☐ Relative humidity control
- ☐ Use of vented cans
- ☐ Dedicated vault storage
- ☐ Proper projection & handling
- ☐ None

Q13 Do you have the occasion to transport nitrate film?

- ☐ Yes
☐ No

Q14 Have you been trained in the packaging and shipping of nitrate?

- ☐ Yes
☐ No

Q15 What has prevented you from receiving training and certification? (please select all that apply)

- ☐ Money
☐ Time
☐ Availability
☐ Lack of institutional support
☐ Other _____

Q16 Has the perception of nitrate film as dangerous or the difficulty of dealing with regulations caused you to not accept or deaccession nitrate film in good condition?

- ☐ Yes
☐ No

Q17 How have you learned about nitrate? (please check all that apply)

- ☐ University-level education or training
☐ On-the-Job training
☐ Workshops
☐ Conferences
☐ Books or articles
☐ Listserv discussions
☐ Casual conversation with peers

Q18

	Not confident at all (1)	A little confident (2)	Somewhat confident (3)	Confident (4)	Very confident (5)
How confident do you feel about your knowledge of nitrate?	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>

Q19 Have you had any direct experience with nitrate fires?

- ☐ Yes
- ☐ No

Q20 Please briefly describe your experience with nitrate fires.

Q21 Have any nitrate films in your collection noticeably deteriorated over time?

- ☐ Yes
- ☐ No

Q22 What steps did you take upon noticing the deterioration of nitrate?

Q23 To what do you attribute the lack of noticeable deterioration of your nitrate collection?

Q24 What kind of knowledge would be most useful to convert into practice? What information would be helpful to you in your storage and handling of nitrate?

Q25 What are the obstacles to overcoming your management and care of nitrate film in your institution's collection (please check all that apply)

- ☐ Lack of Staff
- ☐ Lack of appropriate training for staff
- ☐ Lack of appropriate housing for these materials
- ☐ Lack of funds for appropriate care and conservation of these materials
- ☐ Other (please specify) _____

Q26 What else would you like to see addressed in the NFPA code or see explained in the NFPA code?

AMIA Institutions Surveyed

ID #	Public or Private	Size of Institution	Size of nitrate holdings
1	Public/Private	Unknown	15,000 reels
2	Public	Approx 3000 employees, \$465 operating budget	130,000 reels
3	Private	Less than 100 employees	23,697 reels
4	Private	34 employees	16,000 reels
5	Public	3500 employees	90 reels
6	Private	1 employee	34 reels
7	Public	150 employees	28,000 reels
8	Private	2 employees	200 reels
9	Public	Unknown	50 reels
10	Private	12 employees, \$500,000 operating budget	0 reels
11	Public	8 permanent employees + 1 full-time temp, 5-10 students/volunteers	18,500 reels
13	Public	12 employees	29 reels
14	Public	54 employees	6,600 reels
15	Public	60 employees	136,000 reels
16	Private	45 employees	30 reels

CoSA Institutions Surveyed

ID #	Public or Private	Size of Institution	Size of nitrate holdings
12	Public	60 employees, 10 employees handling nitrate; \$6 million operating budget	40/76 reels; 260 cu ft - 13,000 still negs
17	Public	1 employee handling nitrate	0 reels; 2 cu ft
18	Public	1 employee handling nitrate	35 reels; 5,236 items
19	Public	3 employees handling nitrate	22 reels
20	Public	2 employees handling nitrate	15 reels; unknown cu ft
21	Public	9 employees handling nitrate	65 reels; 7 cu ft
22	Public	2 employees handling nitrate	4 reels
23	Public	2 employees handling nitrate	0 reels; 5 cu ft
24	Public	1 employee handling nitrate	1 reel
25	Public	4 employees handling nitrate	10 reels; 1 cu ft
26	Public	1 employee handling nitrate	1,100 reels; 150 cu ft
27	Public	0 employees handling nitrate	No Nitrate Holdings
28	Public	0 employees handling nitrate	No Nitrate Holdings
29	Public	0 employees handling nitrate	No Nitrate Holdings
30	Public	1 employee handling nitrate	6 reels; 500 or fewer sheets
31	Public	2 employees handling nitrate	2 reels; 3000 cu ft
32	Public	1 employee handling nitrate	0 reels; less than 5000 cu ft
33	Public	3 employees handling nitrate	0 reels; 8905 still negatives
34	Public	2 employees handling nitrate	1 reel; 9 cu ft
35	Public	1 employee handling nitrate	Undetermined # of reels; 200 items
36	Public	4 employees handling nitrate	0 reels; unknown cu ft

Survey of Archival Practices

Survey Background:

The Wisconsin Nitrate Project includes a survey to learn about prevailing practices within the archival community for the management of nitrate film collections. An online questionnaire and polling protocol was created by the Archives Group members of the grant project, comprised of personnel from the Wisconsin Center for Film and Theater Research, the Wisconsin Historical Society, and the Department of Communication Arts. Our questions focused on determining the type of archival institution; the size of the nitrate collection at that institution; the institution's day-to-day practices for nitrate storage, handling, and shipping; and the knowledge or experience of nitrate held by that institution's personnel.

Constituencies:

For purposes of our inquiry, the relevant archival community is considered to be comprised of two complementary constituencies: those archivists and institutions that work primarily with audio-visual materials and which might be expected to manage a large film collection, including nitrate film; and archivists and institutions for which the audio-visual collection may be only a small part of the archive's holding and not central to its mission, but which may nevertheless have some nitrate in the collection. Representatives of these constituencies could be contacted through their respective professional organizations: the Association of Moving Image Archivists and the Council of State Archivists. Questionnaires, included at the end of this document, were sent to the two constituencies.

The Association of Moving Image Archivists (AMIA) is an organization of archivists, collectors, historians, and filmmakers who work primarily, if not solely, with moving image materials in a variety of formats. Within AMIA, there is a Nitrate Committee made up of members who work with and are responsible for collections of films on nitrate. The survey was sent to the AMIA members of the Nitrate Committee, which numbers around 100 members. A total of 15 responses were received; 14 responses came back through the online survey and one institution submitted its answers via email. Repositories represented included public and private institutions ranging in size from one employee to approximately 3,000 employees. Holdings range between 1,000 reels to approximately 2 million reels. A majority of respondents held between 10,000 and 100,000 reels of nitrate moving image film.

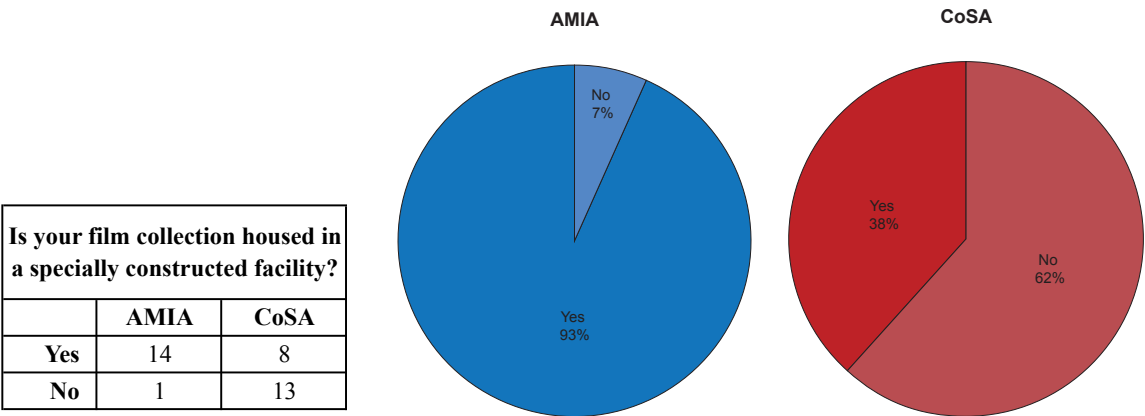
The second group polled was the Council of State Archivists (CoSA), the member group for state archives. State archives generally hold permanent records from their respective state governments, but may also hold manuscript collections that are not government records, as well as collections encompassing all formats. While many have film, videotape, and photographs in their holdings, their focus and training is not usually moving image materials. There are a total of 51 archives represented by CoSA, 21 of which responded to our survey. Of these 21 respondents, 12 institutions have nitrate moving image film. Eleven of the 12 have collections of less than 100 reels; one institution has 1,110 reels of nitrate film. At least 13 of the 21 institutions have still nitrate photograph negatives ranging from a few items to 13,000 nitrate negatives.

We understand that the AMIA group represents archivists who have experience and sophistication when it comes to dealing with nitrate holdings. Our interest in the CoSA group, therefore, was to see how the larger, more general archives community deals with the nitrate in their own collections. Our polling results yielded some revelatory divergences between the two groups in terms of storage and preservation practices. The report that follows compares the two constituencies on parallel questions.

Survey Results:

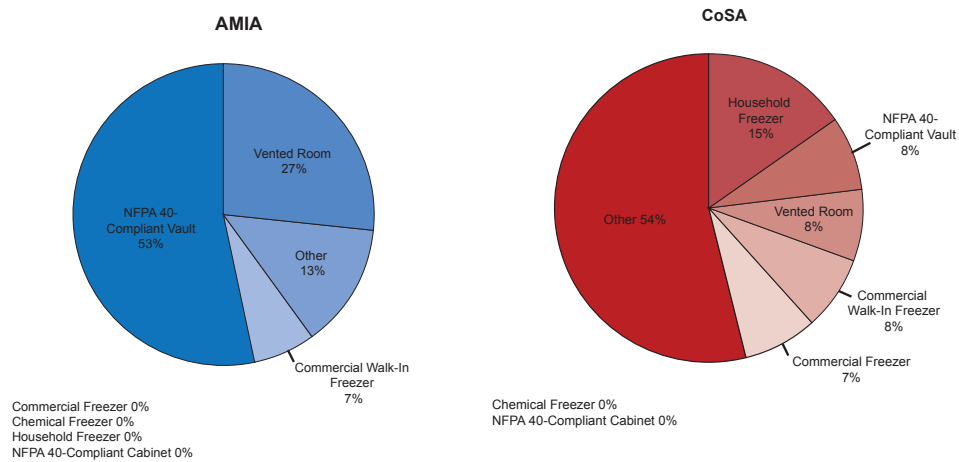
Storage:

The survey found that among AMIA respondents, overwhelmingly (93%), film collections were housed in a specially constructed storage facility. By contrast, the majority of respondents from CoSA (62%) reported that their repositories' film holdings were not housed in any specially constructed facility.



AMIA and CoSA representatives were then asked to select their type of storage facility based on some common options. It is notable that the majority of AMIA respondents (53%) identified a dedicated film vault, while only 8% of CoSA respondents mentioned the equivalent. The CoSA respondents sometimes listed multiple options, and 54% described their storage facility as “Other.” These results suggest the varied storage arrangements in the CoSA community in particular.

Which of the following best describes the storage for your film collection?		
	AMIA	CoSA
Household freezer	0	4
Commercial freezer	0	2
Commercial walk-in freezer	1	2
Chemical freezer	0	0
NFPA 40-compliant vault	8	2
NFPA 40-compliant cabinet	0	0
Vented room	4	2
Other	2	14

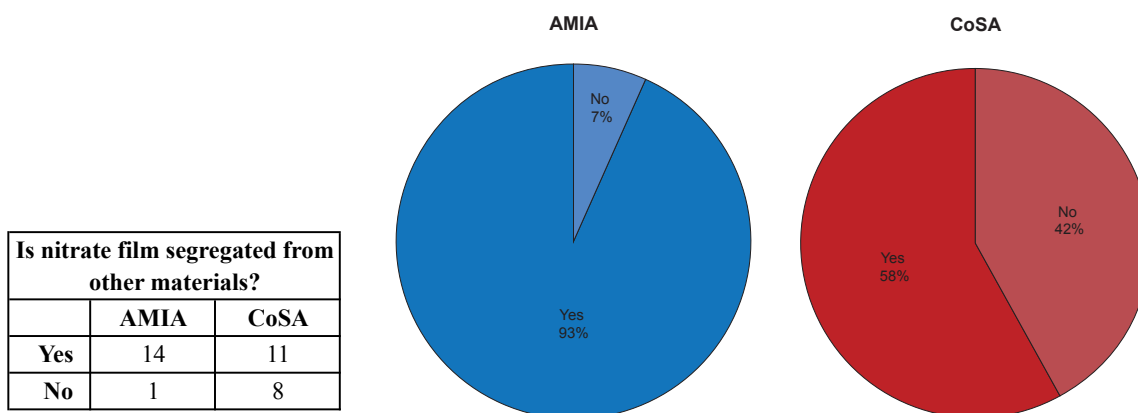


Respondents also had the option of describing their storage facilities.

Descriptions of Storage Facilities from AMIA Respondents	
Institution #6	Temperature and humidity controlled vented room
Institution #7	Vaults, come climate and humidity controlled, some not
Institution #9	Nitrate vaults
Institution #16	Vented room: vault

Descriptions of Storage Facilities from CoSA Respondents	
Institution #12	Non-NFPA 40-compliant vault; some household freezer, some segregated room, some mixed in general archives collection
Institution #17	Air conditioned, concrete basement w/ halon fire-suppression system
Institution #20	Vault with colder than regular building temperatures
Institution #21	Archival repository kept at 60 degrees and 40% relative humidity
Institution #22	Separate climate and humidity controlled vault
Institution #23	General stack area
Institution #24	Cold Storage vault with microfilm holdings
Institution #27	Dedicated general archives storage space with climate control for general collections preservation
Institution #28	Our silver halide microfilm is stored in an environmentally controlled vault
Institution #30	Environmentally controlled "quarantine room"
Institution #32	Standard archives storage area
Institution #33	Stacks designed for storage of paper: approx. 55 degrees F, 43% RH
Institution #35	Only nitrate stock is kept in freezer
Institution #36	Stack storage 60 degrees and 40% RH

Segregation of nitrate film materials appears to be a common practice across all types of repositories, as 93% of AMIA and 58% of CoSA respondents reported this practice as a basic preventive measure.

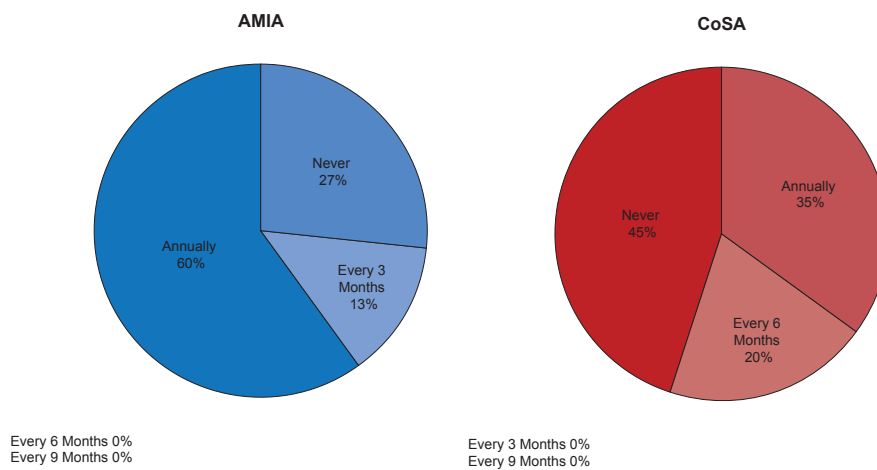


Inspection:

Regular inspection of holdings, however, seems to vary widely by institution. While a majority of AMIA respondents (60%) stated that they made annual inspections of their nitrate holdings – and 13% inspected even more frequently – a handful of respondents (27%) stated that no regular

inspections were done for nitrate holdings specifically. Institutional type may influence the decision to make regular inspection a priority even more. The largest segment of CoSA respondents (45%) stated that no regular inspection of nitrate film holdings occurs, while 35% stated that annual inspection occurred in their institution.

How often do you physically inspect your nitrate holdings?		
	AMIA	CoSA
Never	4	9
Every 3 months	2	0
Every 6 months	0	4
Every 9 months	0	0
Annually	9	7



Respondents also had the option of describing their nitrate inspection processes.

If you have an established procedure for inspecting your nitrate, please describe it briefly

AMIA Respondents	
Institution #1	Open can, remove roll and visually look for signs of decomposition and rust in the can, return to can
Institution #2	Cans are removed from shelves and opened. Staff look for tell-tale signs of nitrate deterioration - funky odors, rust on the inside of the can lids, presence of nitrate dust or "honey" etc. Info is added to our collection management database and reported to curatorial staff
Institution #3	We pull the material with the oldest inspection date from the vaults and inspect them on a workbench. We make condition notes to be added to our paper filing system as well as our cataloging system. We check the level of decomposition based on FIAF codes and make notes of any color process, scratches, dirt, and damage to the film. We also check edge codes and completeness of the element
Institution #4	Reversing the wind, taking condition and credit notes for each reel. Removing decomposition if necessary
Institution #6	Visual and any question of stability a touch of the tongue, if it's bitter, it's starting to decomp.
Institution #8	Yes, according to deterioration levels as described by FIAF and elsewhere
Institution #9	Very detailed inspection report, by hand
Institution #11	Every year we host FLIP, an event where volunteers open every can of nitrate, flip over the reel, and check for obvious signs of decomposition on the reel or interactions with the can. Flagged reels are labeled "TBP" (to-be-printed) and segregated to a different shelf. They are also brought back for full inspection by our nitrate archivist. In addition, inspection is done on-demand every time a reel is requested for a client or for internal use.
Institution #13	We check the reels for any signs of decomposition.
Institution #14	We continually check all of our nitrate cans by winding through every roll. Since we had to reduce staff we don't know yet how long it takes to go through the collection like this (perhaps 2 years?). Additionally, employees where our nitrate is deposited open every can each year to check for signs of nitrate decay on the surface of the film rolls.
Institution #15	Open each can of film. Lift the roll from the can to check both sides of the reel for signs of deterioration. Segregate from the collection if item is found to be deteriorating.

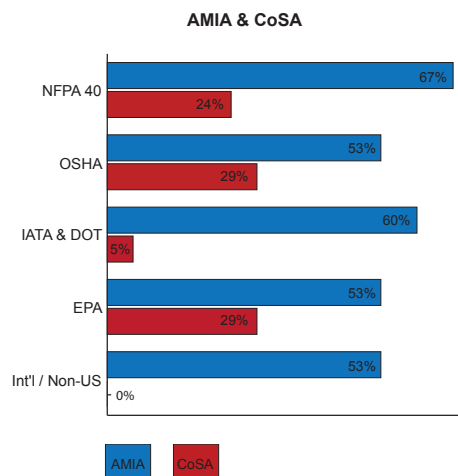
If you have an established procedure for inspecting your nitrate, please describe it briefly

CoSA Respondents	
Institution #12	We did an item level inspection on a rewind in 2010, and as new nitrate films are discovered, housed for freezing, or problems are noted they are inspected again. It's unlikely that there will continue to be annual evaluations of nitrate holdings in the future, nor was that the practice before 2010.
Institution #18	We have a checklist for each collection that determines deterioration levels
Institution #20	Open film cans - check for odors, color changes, stickiness
Institution #30	I have it as a recurring item on my calendar
Institution #32	Arbitrary physical inspection of storage boxes
Institution #34	Since it is stored in a freezer, it is inspected only when needed for duplication or scanning
Institution #35	Photographic materials are inspected upon receipt. Nitrate materials are segregated at that time. Visual inspections are made annually after that.

Regulatory Agencies:

AMIA and CoSA were then asked which regulatory agencies may have influenced their institutional policies on storage, handling, or shipping. The AMIA delegation reported a greater variety of relevant agencies and a higher level of regulatory influence.

In your handling of nitrate, do you consult and are you influenced by the guidelines for any of the following regulatory organizations? (please select all that apply)		
	AMIA	CoSA
NFPA 40 (storage and playback)	10	5
OSHA (employee health/respiratory safety, mandated training)	8	6
IATA & DOT (shipping)	9	1
EPA (disposal)	8	6
International / Non-American organizations	8	0

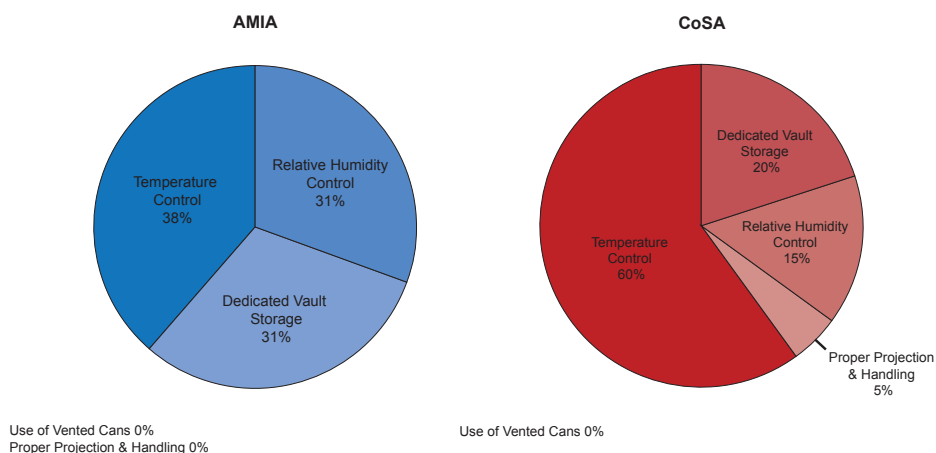


Preservation:

Respondents were given a list of five factors (temperature control, relative humidity control, use of vented cans, dedicated vault storage, and proper projection and handling) that play a role in minimizing risk and maximizing preservation for nitrate film, and were asked to rate them, on a scale of 1 to 5, from most important to least important.

There was a fair amount of agreement between AMIA and CoSA respondents as to which of these factors were more important. As indicated in the graphs below, a plurality of AMIA respondents (38%) and the majority of CoSA respondents (60%) stated that temperature control was the most important factor. Among the rest of AMIA respondents, 31% claimed RH was most important and 31% claimed vault storage was the most important. Of CoSA respondents, 20% said that vault storage was most important, 15% said RH was most important, and 5% said proper projection and handling was most important.

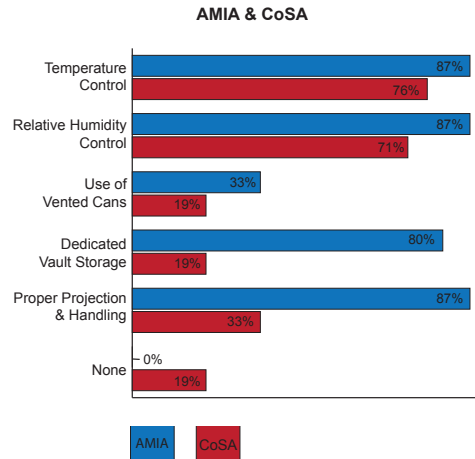
Please rank the following (on a scale from 1 to 5) in terms of what you understand to be the most important conditions for minimizing risk and maximizing preservation for nitrate film.		
	AMIA	CoSA
Most	Temperature Control (38%)	Temperature Control (60%)
2nd	Relative Humidity (31%) / Temperature Control (31%)	Relative Humidity Control (55%)
3rd	Dedicated Vault Storage (54%)	Use of Vented Cans (45%)
4th	Proper Projection & Handling (54%)	Dedicated Vault Storage (40%)
Least	Use of Vented Cans (62%)	Proper Projection & Handling (75%)



Both AMIA and CoSA respondents selected RH as the second most important factor, but AMIA respondents were more divided over whether RH or temperature were more important.

The majority of CoSA respondents reported being able to meet those criteria deemed most important: temperature control (76%) and relative humidity control (71%). The majority of AMIA respondents (80% or more) reported being able to meet all of the criteria, with the exception of vented cans. However, given that many AMIA respondents did not think vented cans were an important factor, these data might reflect a decision not to use them, rather than an actual inability to secure them. Nineteen percent of CoSA respondents reported that they were not able to meet any of the conditions.

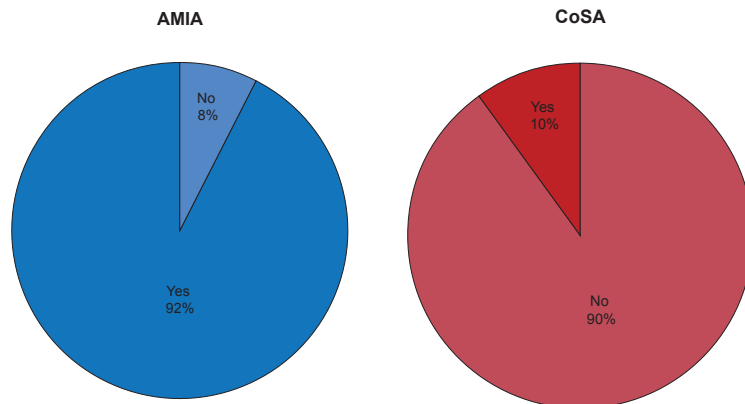
Which of the following categories for minimizing risk and maximizing the preservation of nitrate film is your facility able to meet? (please select all that apply)		
	AMIA	CoSA
Temperature control	13	16
Relative humidity control	13	15
Use of vented cans	5	4
Dedicated vault storage	12	4
Proper projection & handling	13	7
None	0	4



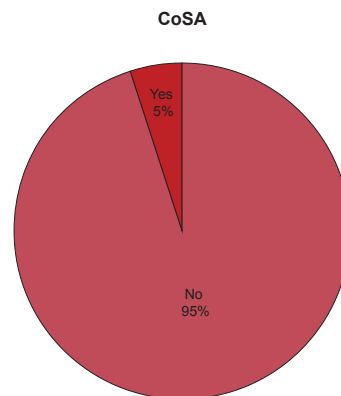
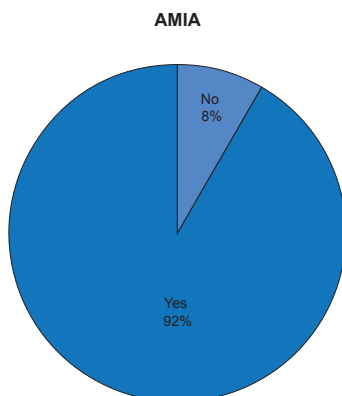
Packaging and Shipping:

The survey also asked about options among institutions in regards to packaging and shipping of nitrate film, and about training in this area. Among AMIA respondents, the vast majority (92%) report having had an occasion to transport nitrate film. The same percentage report receiving some level of training in the packaging and shipping of nitrate. By contrast, the majority of CoSA respondents (90%) had never had an occasion to transport nitrate film. This seemed to correspond to the percentage of respondents that had also never received training or certification in the packaging and shipping of nitrate (95%), a logical correlation.

Do you have the occasion to transport nitrate film?		
	AMIA	CoSA
Yes	12	2
No	1	18

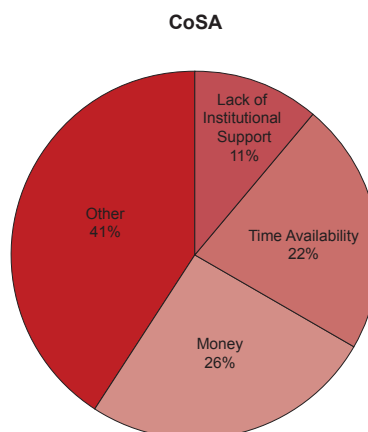


Have you been trained in the packaging of nitrate?		
	AMIA	CoSA
Yes	11	1
No	1	19



The reasons given for lack of training in this area (chiefly by the CoSA respondents, who were also given the option of citing more than one factor) was that these duties lay outside of the respondent's professional responsibilities; that the packaging and shipping was handled by another department; or that the institution simply did not package and ship these materials at all.

What has prevented you from receiving training and certification? (please select all that apply)		
	AMIA	CoSA
Money	0	7
Time Availability	0	6
Lack of institutional support	0	3
Other (please specify)	1	11



Some respondents elaborated on the reasons why they had not been trained and certified in the shipping of nitrate materials.

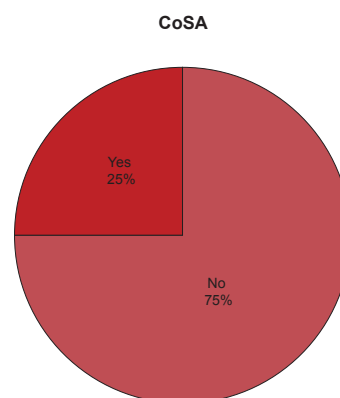
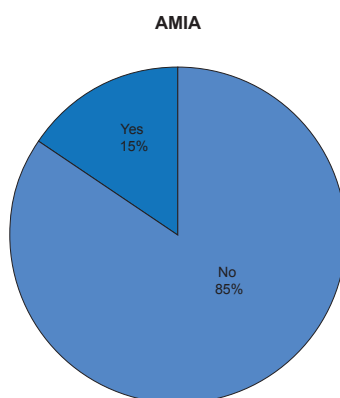
What has prevented you from receiving training and certification?	
AMIA Respondents	
Institution #14	Shipping is handled by another organization

What has prevented you from receiving training and certification?	
CoSA Respondents	
Institution #18	We don't ship
Institution #19	Another employee has been involved in this. I think the thing that has prevented her from being certified are the constantly changing regulations
Institution #20	We are under staffed, under funded and not a priority in the overall scheme of things until recently
Institution #23	Other priorities
Institution #24	Limited materials in the collection
Institution #26	We use off-site storage and have nitrate shipped directly to the service provider. Beyond what we had initially , everything since then goes directly to the third party
Institution #27	We hold no nitrate film
Institution #31	Didn't know there was a certification program out there! I trained myself using available literature and online training
Institution #32	We do not ship flat film so it is not an issue
Institution #33	There has been no reason to pack and ship nitrate negatives as we digitize still images in house
Institution #34	We don't have the need to ship nitrate film

Perceived Danger:

Perceptions of nitrate as dangerous did not seem to be a concern by either group, as the majority of both AMIA and CoSA respondents (85% and 75%, respectively) stated that this concern would not lead to the rejection or de-accessioning of nitrate film materials.

Has the perception of nitrate film as dangerous or the difficulty of dealing with regulations caused you to not accept or deaccession nitrate film in good condition?		
	AMIA	CoSA
Yes	2	5
No	11	15

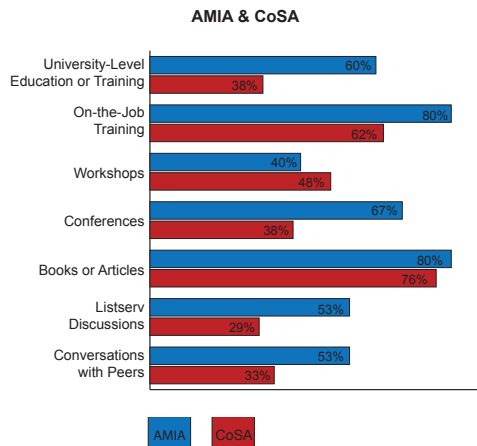


Background Knowledge:

There appeared to be some commonalities between the two groups in how knowledge about nitrate materials was gained. AMIA respondents reported that on-the-job training and books or articles were the chief sources of their current knowledge about how to handle these

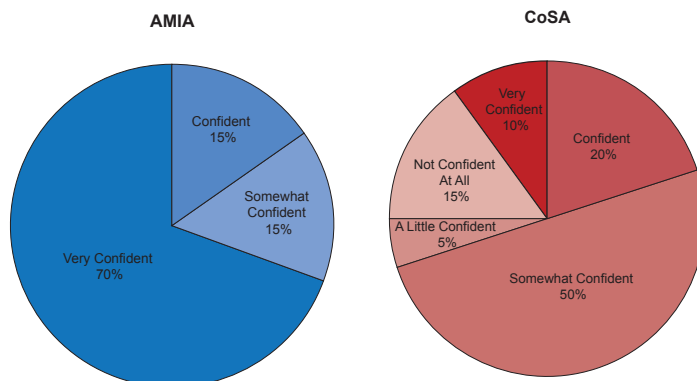
materials. Similarly, CoSA respondents most frequently cited books and articles as their means of gaining knowledge on the topic, followed by on-the-job training. The largest differential was university-level education or training: while 60% of AMIA respondents cited higher education as a source of knowledge about nitrate, only 38% of CoSA respondents reported gaining information in this way.

How have you learned about nitrate? (please check all that apply)		
	AMIA	CoSA
University-level education or training	9	8
On-the job training	12	13
Workshops	6	10
Conferences	10	8
Books or articles	12	16
Listserv discussions	8	6
Casual conversations with peers	8	7



Respondents had the opportunity to self-report on their level of confidence in their knowledge of nitrate. All respondents from the AMIA group selected “somewhat confident,” “confident,” or “very confident.” However, while a majority (80%) of the CoSA group felt “very confident,” “confident,” or “somewhat confident,” 15% felt “not confident at all” about their knowledge of nitrate.

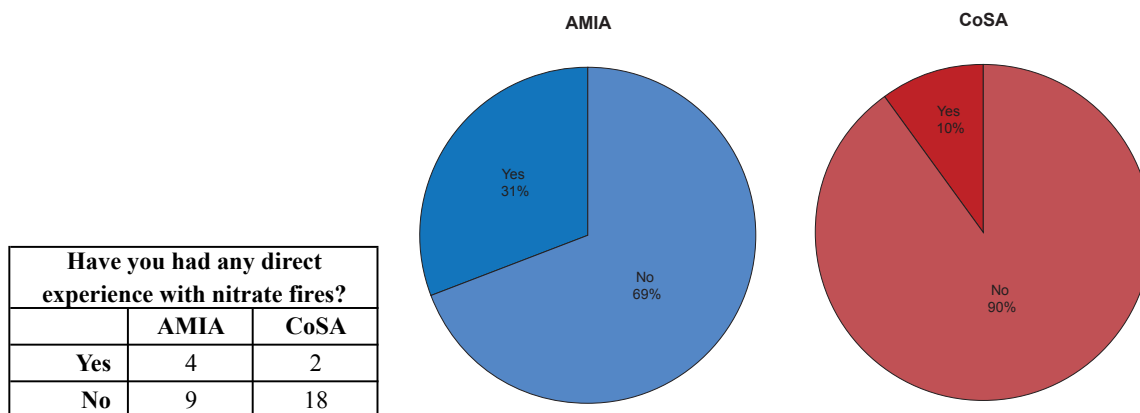
How confident do you feel about your knowledge of nitrate?		
	AMIA	CoSA
Not confident at all	0	3
A little confident	0	1
Somewhat confident	2	10
Confident	2	4
Very confident	9	2



A Little Confident 0%
Not Confident at All 0%

Fires:

The majority of respondents in both groups (69% for AMIA and 90% for CoSA) stated that they had not had direct experience with nitrate fires.



When asked to describe their experience with nitrate fires, then, only a few respondents had incidents to report, and three of the AMIA responses involved controlled burns.

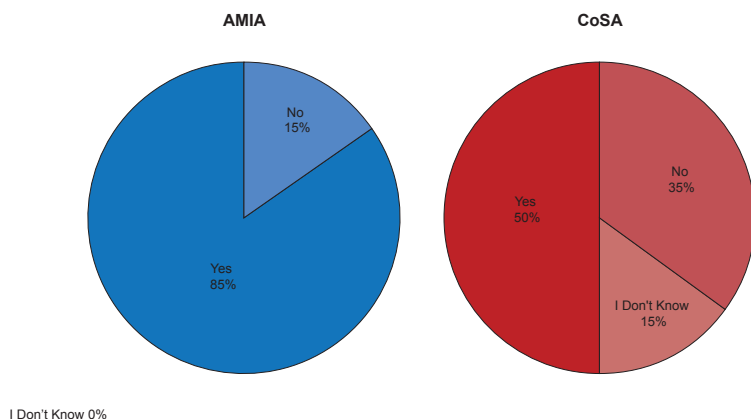
Please briefly describe your experience with nitrate fires	
AMIA Respondents	
Institution #3	I will burn a small piece (about 5 ft of material) in a metal can in my parking lot to show my students the impact a nitrate fire could have on an archive. I do this once a year.
Institution #6	In 68 years of handling nitrate I've never even come close to a fire, only when burning wasted prints.
Institution #9	Test burns, in order to feel comfortable working with it.
Institution #15	#1. Film handling: static electricity while reel was being wound on motor rewind at high speed caused spark and fire. Reel burned out and work area damaged, but no one hurt. Handling procedures changed to enforce hand-winding at low speed. (Note: that static electricity was the cause of this fire is a point of dispute.) #2. Film storage: one reel self-ignited w/in can during a hot weekend. Sprinkler system protected other reels except for one can sitting on top of burned film. Only two reels lost, and no one hurt. #3. Film storage/handling: While rearranging cans in vault, staff member felt a hot can. Followed procedure by dropping can and locking vault. Film burned out inside container w/o triggering sprinklers. No further damage and no one hurt. #4. Film projection: Film stopped in gate of Norelco FP-20 projector likely due to bad splice. Film ignited and burned several feet before projector stopped automatically. Fire contained w/in projector but destroyed rear element for lens, runner strips, and skate. Did not spread further and no one hurt. Booth and projector are NFPA 40 compliant and approved by Fire Marshal. #5. Film projection: splice came apart as film went through gate and shot out of small slot in the door and back into lamphouse where it started to burn. Picture stayed on screen but no sound. Operator stopped machine, which extinguished fire. No one was hurt. Booth and projector are NFPA 40 compliant and approved by Fire Marshal.

Please briefly describe your experience with nitrate fires	
CoSA Respondents	
Institution #12	Worked at New York Historical Society in 2003, where there was a fire from a reel of nitrate film that was in a vented can and considered in good shape. Was particularly influenced against the idea of retaining nitrate prints at the time because of the destruction done to many other collections for the sake of erratically unstable film. I feel less inclined against retaining nitrate as I learn more, however.

Deterioration:

Sizeable percentages of both AMIA and CoSA respondents (85% and 50%, respectively), however, reported noticeable deterioration of their nitrate materials over time.

Have any nitrate films in your collection noticeably deteriorated over time?		
	AMIA	CoSA
Yes	11	10
No	2	7
I Don't Know	0	3



The two groups were asked about the steps taken in response to signs of nitrate deterioration and provided a variety of responses. Fairly consistently, though, respondents described removing the deteriorated nitrate from the rest of the collection to be either copied or destroyed, depending on the institution's policies or capabilities.

What steps did you take upon noticing the deterioration of nitrate?	
AMIA Respondents	
Institution #1	We alert the curatorial staff as to the condition of the nitrate, monitor the film, and if necessary, recommend to destroy the roll
Institution #2	Deteriorated sections removed and disposed of as hazardous waste. Remaining sections of the film were evaluated for possible preservation copying, and if determined to be appropriate, this is done. Film goes back into storage. In general terms, our storage conditions are so good that the primary level of deterioration of the films happened outside of our control. Films that have been in our control are generally very stable and not obviously deteriorating.
Institution #3	Contacted the curator about the conditions and asked for approval to remove any sections that were no longer able to wind through. This is documented in our cataloging records. If the material is completely deteriorated, I ask the board of trustees for formal approval to de-accession the item from the collection.
Institution #4	Deteriorated nitrate was removed and properly disposed of. This mostly happened before the nitrate was moved to our cold storage vault in 2008.
Institution #6	Contact the appropriate archive
Institution #7	Loose winding. We cut-off the bad parts (too sticky to unwind) and throw them away. In the future, I hope to get a drying cabinet (simple cupboard with wire shelves and strong airflow)
Institution #9	We are a full-service motion picture photochemical lab, so we preserve and restore it
Institution #11	Deteriorated films are marked "TBP" (to-be-printed), and if preservation funding can be secured from a grant or a private donation (we have a modest endowment), it is copied. We have much more film than we can copy, and prioritize based upon curatorial assessment of content and condition. We remove sections of film where the image is already lost if the remainder can be salvaged, and discard film that has reached the last stages of decomposition.
Institution #14	We removed the deteriorated parts and tried to salvage the rest of the film. If this wasn't possible, the nitrate was disposed.
Institution #15	After deteriorated elements are segregated from collection, a list of these items with title and element description is submitted to curator, archivist, and preservationists. Depending on a set of values, which include rarity, vintage (earliest generation), historical importance, etc., some items are selected and cued-up for duplication, while others have the deteriorated section(s) removed before returning to storage.
Institution #16	Placed in specialized cold storage.

What steps did you take upon noticing the deterioration of nitrate?	
CoSA Respondents	
Institution #12	A film preservation intern surveyed our nitrate moving image collection in 2008 and again in 2010. Some films have deteriorated considerably. We discarded fused film, made plans to digitize some damaged film, and placed others in freezers. We routinely weed fused still negatives, when we come across them.
Institution #25	Scanned and put in freezer
Institution #26	We attempt to arrest the deterioration and then seek to restore/conservate what we can.
Institution #29	All nitrate negatives in our holdings were reformatted onto safety film
Institution #30	Deaccessioned and destroyed
Institution #31	Froze it
Institution #33	Alerted management to issue. Began a program to digitize negatives
Institution #35	Reformatting
Institution #36	Copying the still film negatives to preserve the historical image

Those respondents who had not noticed deterioration most commonly cited proper storage conditions as the reason.

To what do you attribute the lack of noticeable deterioration of your nitrate collection?	
AMIA Respondents	
Institution #5	We have a very small and stable collection. Our reels are actually stored at LoC in their vaults and we inspect them very infrequently. During that time, we've not noticed any new or additional decomposition.

To what do you attribute the lack of noticeable deterioration of your nitrate collection?	
CoSA Respondents	
Institution #18	Temperature and humidity control, freezers
Institution #20	The vault where they are stored has not been subject to major temperature and humidity changes, even though the proper temperatures and humidity have not been maintained
Institution #24	Consistent temperature and humidity control
Institution #25	In the freezer
Institution #26	Institutional lack of knowledge (early)
Institution #30	Prior storage without environmental controls
Institution #31	We have an excellent walk-in freezer and the items are in sealed packages
Institution #32	Control of temperature and RH. Good air circulation
Institution #34	Storage temps and RH
Institution #35	Proper environmental controls
Institution #36	Good storage conditions (not the best, but very good). Lack of handling, etc.

Respondent Recommendations:

Both respondent groups identified a number of priorities for knowledge and education in the area of nitrate film. AMIA respondents stated three priorities in particular: eliminating rumors and folklore about working with nitrate, real data about “the brown powder,” and a simple fact sheet on how to package and ship materials. CoSA members are very interested in guidelines and

information on identifying nitrate film – particularly flat photographic nitrate negatives which are more likely to be found in non-moving image archives than nitrate moving image film.

What kind of knowledge would be most helpful to convert into practice? What information would be helpful to you in your storage and handling of nitrate?	
AMIA Responses	
Institution #1	Eliminate false rumors and folklore about nitrate and nitrate storage.
Institution #2	Real data about the stages of deterioration and whether nitrate "brown powder" is actually flammable or explosive, what are the true circumstances regarding nitrate that might lead to fires due to "spontaneous" combustion, and absolutely debunking the myth that nitrate film is ever shock sensitive
Institution #4	Proper/regular inspection of all nitrate holdings, returning the cans back to the proper (cold) storage
Institution #7	A simple "how to ship nitrate" facts sheet - valid for Europe and USA, air and land transport
Institution #9	What collections/archives have the most critical needs?
Institution #11	Any way to bring down the cost of shipment and storage would be appreciated. It would also be great to know more about health hazards. Obviously, we would also want to know if the health and safety risks were more elevated than previously thought.
Institution #14	It would be great if the FIAF Treasures database gave more detailed information about the preservation status of films shot on nitrate stock. This way it would be easier to decide if we should preserve a title from our own collection since this isn't always necessary if the title is preserved at another archive.
Institution #15	Although we recognize and respect the hazardous characteristics of nitrate film, our experience tells us that the powder generated by deteriorating nitrate is not shock sensitive or explosive, as described in the current MSDS. We are not sure what effect it would have on the handling and disposal of nitrate film if this assertion could be disproven, but it would be most helpful to know for sure what real danger it actually poses to the staff, our collection, and the environment.
Institution #16	Comprehensive environmental information (beyond temperature and humidity concerns)

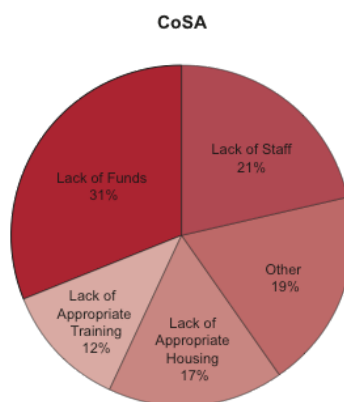
What kind of knowledge would be most helpful to convert into practice? What information would be helpful to you in your storage and handling of nitrate?	
CoSA Responses	
Institution #12	Whether to freeze or to vent? (storage practices that minimize risk of deflagration)
Institution #18	How to identify, preserve, and store. Levels of deterioration
Institution #20	Proper identification of nitrate films, proper storage and handling practices and procedures, etc.
Institution #22	Information about the projection of nitrate film would be helpful
Institution #24	Reformatting of nitrate film; stages of deterioration to watch for
Institution #25	Ability to recognize it
Institution #26	We out-source most of that service
Institution #31	I'd like to know more about national standards
Institution #33	Brief directions in plain English - no more than one page
Institution #35	Better acuity in visual identification of nitrate film stock
Institution #36	From time to time I have need to ship film, but as I am not certified and cannot get anyone certified to ship for me, it remains in our excellent vault storage / segregated from other material.

The survey sent to CoSA also asked what changes the respondents would like to see made to the NPFA-40 code governing nitrate film. While few respondents answered this question, those that did requested a better method for storing nitrate and attention to nitrate sheet film.

What else would you like to see addressed or explained in the NFPA code?	
Institution #12	an intermediate and achievable method for storing nitrate
Institution #20	Not sure, don't have enough knowledge of the subject matter to comment
Institution #31	can't think of anything
Institution #32	The code only addresses the roll film. It needs to be updated to also addresses sheet film issues.

CoSA respondents were also asked about the obstacles they faced in their management and care of nitrate materials, such as a lack of staff, lack of training, lack of housing, or lack of funds. Respondents were able to select multiple answers, and the results point toward a variety of issues facing these institutions, with no one obstacle emerging as the most significant.

What are the obstacles to overcoming your management and care of nitrate film in your institution's collection?	
Lack of staff	9
Lack of appropriate training	5
Lack of appropriate housing	7
Lack of funds	13
Other	8



It is also important to note that 70% of CoSA respondents did not feel very confident in their knowledge of nitrate film – both flat photographic negatives and moving image nitrate film. This is an area AMIA members can and should address by doing educational outreach to non-moving image archivists via conferences, workshops and webinars.

Appendix 2: Visual Inspection Process

1. Blank inspection sheet
2. Inspection sheet for Stage 0 sample
3. Inspection sheet for Stage 2 sample
4. Inspection sheet for Stage 4 sample

Physical Inspection Sheet

Inspected By
Sample ID

Date of Inspection
RTI Yes or No

DMin

DMax

DSprocket

Thickness

Condition Level:

0 = none

1 = Light (less than $1/3^{\text{rd}}$ of frame affected)

2 = Moderate ($1/3^{\text{rd}}$ – $2/3^{\text{rd}}$ frame affected)

3 = Heavy (more than $2/3^{\text{rd}}$ frame affected)

1 scratch = .05 mm

Base Condition

Scratch Count:

Vertical

Horizontal

Brittleness:

Softness:

Yellowing: Yes or No

Image Condition

Scratch Count:

Vertical

Horizontal

Stickiness:

Faded/Bleached:

Amount of Image Gone (in mm):

Physical Damage

Buckle

of Sprockets Broken

Tears

Folds

Foreign Matter

Dirt

Grease/Oil

Brown Powder

Adhesive residue

Notes:

Physical Inspection Sheet

Inspected By ALM
Sample ID 1-0-1935-41

Date of Inspection 1/24/13
RTI Yes or No

DMin .91

DMax 2.07

DSprocket .18

Thickness .062

Condition Level:

0 = none

1 = Light (less than 1/3rd of frame affected)

2 = Moderate (1/3rd - 2/3rd frame affected)

3 = Heavy (more than 2/3rd frame affected)

1 scratch = .05 mm

Base Condition

Scratch Count:

Vertical .3 mm

Horizontal 0 mm

Brittleness: 0

Softness: 0

Yellowing: Yes or No

Image Condition

Scratch Count:

Vertical .05 mm

Horizontal 0 mm

Stickiness: 0

Faded/Bleached: 0

Amount of Image Gone (in mm): 0 mm

Physical Damage

Buckle 0

of Sprockets Broken 0

Tears 0

Folds 0

Foreign Matter

Dirt 0

Grease/Oil 0

Brown Powder 0

Adhesive residue 0

Notes:

Physical Inspection Sheet

Inspected By ALM
Sample ID 2.2-1919-24

Date of Inspection 2/4/13
RTI Yes or No

DMin .14 DMax .84

DSprocket .17

Thickness .060

Condition Level:

0 = none

1 = Light (less than 1/3rd of frame affected)

2 = Moderate (1/3rd - 2/3rd frame affected)

3 = Heavy (more than 2/3rd frame affected)

1 scratch = .05 mm

Base Condition

Scratch Count: Vertical 19m Horizontal .10m

Brittleness: 1 Softness: 0

Yellowing: Yes or No

Image Condition

Scratch Count: Vertical 18m Horizontal .10m

Stickiness: 0 Faded/Bleached: 0

Amount of Image Gone (in mm): 0m

Physical Damage

Buckle 0 # of Sprockets Broken 0 Tears 0 Folds 0

Foreign Matter

Dirt 2 Grease/Oil 0 Brown Powder 0 Adhesive residue 0

Notes:

brittleness comparative

Physical Inspection Sheet

Inspected By ALM
Sample ID 3-4-1919-50

Date of Inspection 2/6/13
RTI Yes or No (No)

DMin .12

DMax .92

DSprocket .09

Thickness .063

Condition Level:

0 = none

1 = Light (less than 1/3rd of frame affected)

2 = Moderate (1/3rd - 2/3rd frame affected)

3 = Heavy (more than 2/3rd frame affected)

1 scratch = .05 mm

Base Condition

Scratch Count:

Vertical 23m

Horizontal 0m

Brittleness: 1

Softness: 0

Yellowing: (No) Yes or No

Image Condition

Scratch Count:

Vertical 10.6m

Horizontal .15m

Stickiness: 1

Faded/Bleached: 2

Amount of Image Gone (in mm): 3m x 17m

Physical Damage

Buckle 0

of Sprockets Broken 0

Tears 0

Folds 0

Foreign Matter

Dirt 1

Grease/Oil 0

Brown Powder 1

Adhesive residue 0

Notes:

brown powder in can - residue may be dirt +/or bp.

Appendix 3: Detailed Experimental Procedures

1. Detailed experimental procedures for cellulose nitrate accelerated aging experiments

Appendix 2: Detailed Experimental Procedures for Cellulose Nitrate Film Accelerated Aging Experiments

Materials. All chemicals were purchased from Sigma Aldrich (Milwaukee, WI) and used without further purification unless otherwise noted. Elemental analyses of film samples assaying for carbon, hydrogen, nitrogen, and sulfur were conducted by Columbia Analytical (Phoenix, AZ). BAM Fallhammer tests and BAM Friction Tests were conducted by Chilworth Technology, Inc. according to the specifications prescribed by the 2009 *United Nations Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria* (5th edition, 2009; <https://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev5/English/ST-SG-AC10-11-Rev5-EN.pdf>, accessed on Dec. 1, 2015)

Film Sample Preparation. Film frames were subjected to physical and chemical property testing in their native form with any gelatin (or emulsion layer) intact, or they were treated with bleach to remove the emulsion layer to enable testing of the cellulose nitrate base alone. The emulsion layer was removed by treatment with Tough Guy™ ultra bleach for 30 min, followed by exhaustive washing with deionized water and drying under vacuum at 22 °C. We have carefully noted in the text of this report when we have handled native film samples or ones wherein the emulsion layer was removed.

IPI Acidity Test. pH testing on the film was performed according to the method established by the Image Permanence Institute (IPI). Briefly, a 4 mm x 18.5 mm piece (50 mg) of unbleached film was cut and submerged in 5 mL of MilliQ water (> 18 MΩ resistance) in a tightly capped 20 mL scintillation vial. After 24 h at 22 °C, the pH was measured using an EMD colorpHast® pH-indicator strip (pH range 2.0–9.0).

Size-Exclusion Chromatography (SEC). SEC analyses were performed on a home-built system equipped with two Polymer Labs PolyPore 300 x 7.5 mm columns and a Waters 410 Differential Refractometer, operating with DMF with 0.1 M LiBr dissolved as the eluent at a flow rate of 0.8 mL/min. In all analyses, the columns and detector were thermostatted at 70 °C and 50 °C, respectively. A molecular weight calibration curve was constructed either ten narrow molecular weight poly(styrene) standards or seven narrow molecular weight poly(methyl methacrylate) standards ($M_n = 580\text{--}377,400$ kg/mol), in order to determine the molecular weight distributions ($\mathcal{D} = M_w/M_n$) for all of the bleached cellulose nitrate samples (emulsion layer removed). Data was acquired using a NI USB-6008 DAQ (analog to digital converter) and a custom LabView (National Instruments Co.) interface written by Adam Schmitt. The data was calibrated and analyzed using a custom procedure written in Igor Pro (https://figshare.com/articles/Computer_Code_for_Materials_Scientists_Igor_Pro_Procedures_for_Analyzing_Dynamic_Light_Scattering_Rheology_and_Synchrotron_X_ray_Scattering_Data/644515).

¹H NMR. ¹H NMR spectra were acquired in DMSO-*d*₆ or acetone-*d*₆ on an Avance-400 spectrometer operating at 400 MHz with a pulse repetition delay of at least 10 s. Spectra were referenced to the residual protiated solvent peak in each sample. These

spectra were quantitatively integrated in order to determine chemical changes to the structure of the cellulose nitrate film.

Thermogravimetric analysis (TGA). The thermal stability of each cellulose nitrate film was measured in a TA Instruments Q500 Thermogravimetric Analyzer using a ramp rate of 10 °C/min under an O₂ (g) purge (20 mL/min) over a temperature range of 25-250 °C followed by a temperature jump to 600 °C to ensure complete sample combustion. The typical mass of the film sample used for each TGA run was ~3-5 mg.

Differential Vapor Sorption (DVS). Water uptake measurements as function of relative humidity at 30.0 °C and 60.0 °C made using a TA Instruments Q5000SA dynamic vapor sorption analyzer. At each relative humidity condition between 5–95 %RH, the water uptake of the sample was monitored by measuring the mass increase upon equilibration for 20 min. These measurements were made in the laboratory of Prof. M. A. Hickner of the Department of Materials Science Engineering at Penn State University (State College, PA).

Accelerated Aging studies. For each accelerated aging trial conducted at 60 °C and a given relative humidity condition, we prepared one 32 oz., wide-mouth jar equipped with Teflon-lined polypropylene cap. Each jar was loaded with seven (7) 1” x 4” inch borosilicate test tubes. We then made six (6) film packets, each comprising five (5) consecutive film frames of similar condition that were bound together into a stack using Teflon-coated copper wire threaded through the sprocket holes. These packets were intended to mimic a roll of film in a smaller physical footprint format compatible with the oven selected for the elevated temperature, long-term aging experiment. Each of one of these six packets was loaded into a different test tube in the 32 oz. glass jar. The seventh test tube was loaded with a saturated water/salt solution, whereby the use of different salts enabled establishment of different relative humidity conditions within each sealed aging containers. According to literature references from the National Institute of Standards and Technology (NIST), we used MgCl₂, NaBr, and KCl saturated salt-water solutions (~3.0 g of salt in ~12 mL MilliQ water) to produce 30, 50, and 80 % RH environments, respectively, at 60 °C. One sample jar was prepared for each of **CN-0** aged at 30 %RH, **CN-0** at 50 %RH, **CN-0** at 80 %RH, **CN-2** at 80 %RH, **CN-4** at 80 %RH. Note that the **CN-4** jar contained only one stacked film packet, as we sought to test only the 360 day aging time point for this already degraded sample. These five separate jars were loaded into a Thermo Scientific Lindberg Oven equipped with a built-in digital microprocessor for controlling the temperature at $T = 60.0 \pm 0.1$ °C. We monitored the relative humidity at least three times weekly using a NIST-calibrated Fisherbrand hygrometer (Fisher Scientific, Inc.). The measured relative humidity in each container was within ± 5 %RH of the target value. At each time point (15, 30, 60, 90, 180, and 360 days), we carefully removed the glass jar from the oven, opened it in a fume hood to vent any noxious gases, and removed one film sample packet from the container. **CAUTION: Gases evolved in this experiment are toxic! Inhalation of nitric acid vapors can lead to permanent respiratory damage, including permanent loss of the sense of smell.** The remaining samples were left in the container, which was resealed and returned to the 60 °C oven to continue the aging experiment.

Upon removing each film packet from the controlled accelerated aging environment, the samples were stored in Ziploc bags and subjected to testing protocols described above in either their native form (emulsion layer intact) or bleached form (emulsion layer removed) as soon as possible.


Appendix 4: Reports from Chilworth Global


1. Report from Chilworth Global, September 6, 2012
2. Report from Chilworth Global, July 11, 2014

PROCESS SAFETY TEST RESULTS AND INTERPRETATION
FOR
CELLULOSE NITRATE HERITAGE FILM

TO : University of Wisconsin - Madison
Department of Communication Arts
2151 Vilas Hall
821 University Avenue
Madison, WI 53706

F.A.O.: Ms. Heather Heckman

Reviewed By 
.....
Jason Cargill
Acting Laboratory Supervisor

Approved By  For
.....
Don B. Churchwell
Laboratory Manager

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

Report No : R/12948/0912/SS
Date : September 6, 2012
CTI Ref : UN12948RP

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INTRODUCTION

This report presents the results of dust explosibility measurements performed on your **CELLULOSE NITRATE HERITAGE FILM** sample. The results are summarized in Table 1 on the following page. The report includes a description of the test procedures and an interpretation of the results.

Chilworth Technology is experienced in providing specific advice in the areas of dust explosion prevention and control, gas and vapor explosion, electrostatics, thermal stability and chemical reaction hazards. Site visits to discuss operational safety or to perform plant inspection and measurements can be arranged.

TABLE 1

SUMMARY OF TEST RESULTS

For Test Sample: **CELLULOSE NITRATE HERITAGE FILM**

Parameter		Test Results
Fire Risk		
1.	Flammability of Solids - Burning Rate	*
2.	Flammability of Solids @ Elevated Temp.	*
Dust Explosion Risk		
1.	Explosibility Classification	*
2.	Explosion Severity - 20L Sphere	
	Maximum Explosion Pressure (bar)	*
	Maximum Rate of Pressure Rise (bar/s)	*
	Kst Value (bar.m/s)	*
3.	a. Minimum Ignition Energy - Dust Cloud (mJ)	*
	b. Minimum Ignition Temperature - Dust Cloud (°C)	*
4.	a. Limiting Oxygen Concentration (% by volume)	*
	b. Minimum Explosible Concentration (g/m ³)	*
5.	a. BAM Fallhammer Test of Impact Sensitivity (J)	>60
	b. BAM Friction Test of Friction Sensitivity (N)	>360
Thermal Stability		
1.	Bulk Powder Test - Onset Temperature (°C)	*
2.	Aerated Powder Test - Onset Temperature (°C)	*
3.	Air Over Layer Test - Onset Temperature (°C)	*
Electrostatic Risk		
1.	Volume Resistivity	ambient R.H.
	(ohm.m)	low R.H.
		*
2.	Charge Decay Time	ambient R.H.
	(min:sec)	low R.H.
		*

Note: The results given in this report apply to the sample tested. Changes in composition, particle size, and moisture content may affect the results.

* Indicates test was not performed on your sample.

BAM FALLHAMMER TEST
MEASUREMENT RESULTS AND INTERPRETATION
FOR
CELLULOSE NITRATE HERITAGE FILM

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

BAM FALLHAMMER TEST

UN Test 3 (b) (ii)

Introduction

The ignition sensitivity of solids, pastes, and gels to impact can be tested by the BAM Fallhammer Apparatus. [BAM = German Institute for Materials Testing] The method yields quantitative results in the form of a limiting impact energy.

The BAM Fallhammer Apparatus consists of a cast steel block with base, anvil, column, guides, dropweights, release device and impact device. The apparatus is shown in Figure 1. Dropweights of different masses -- 1, 2, 5 and 10 kg -- can be attached to the column and guides and by varying the weights and the height from which they are dropped, the impact energy can be varied from 1 J through to 60 J.

The sample substance being tested is enclosed in a sample cell consisting of two co-axial steel cylinders, one above the other in a hollow cylindrical steel guide ring. The cylinders are steel rollers from roller bearings with polished surfaces and rounded edges. The sample cell is placed on the intermediate anvil and centered.

Test Procedure

Chilworth Technology performs BAM Fallhammer Testing in accordance with the United Nations' (UN) Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.2 - 9/95). Substances are usually tested as received. Wetted substances are tested with the minimum content of wetting agent provided for transport.

A sample is taken with a scoop of 40 mm³. The substance is then placed in the open sample cell, which is already in the locating ring on the intermediate anvil. The upper steel cylinder is then set to be 1 mm above the lower cylinder and is held in that position by means of an O-ring.

When the sample cell is properly positioned, the dropweight is released and the impact result is observed. Distinction is made between "no reaction", "decomposition" (change of color), and "explosion" (crackling, sparking, or inflammation).

The series of trials is started with a single trial at 10 J. If an "explosion" is observed, the series is continued with trials for decreasing impact energies until a "decomposition" result or "no reaction" result is observed. If however, a "decomposition" result or "no reaction" result is observed at 10 J, the weight is slowly increased until an "explosion" result is observed or the maximum impact energy is reached (60 J).

The limiting impact energy for a substance, is defined as the lowest energy for which an "explosion" result is obtained from at least one out of the six trials. The UN Recommendations indicate that a substance is too sensitive for transport if it exhibits a limiting impact energy of 2 J or less.

Results

The results of BAM Fallhammer Testing for CELLULOSE NITRATE HERITAGE FILM sample are shown in Table 1. The limiting impact energy for this sample is >60 Joules. These results indicate that this sample is not particularly sensitive to ignition by mechanical impact.

Company Name	: University of Wisconsin - Madison
Test Powder	: CELLULOSE NITRATE HERITAGE FILM
Ref. No.	: N/A
Origin of the Sample	: N/A
Size Information	: Sample tested as received
Sample Description	: Fine, brown powder

Test Purpose	:	To determine the limiting impact energy of the sample.
Apparatus type	:	BAM Fallhammer Apparatus
Date of test	:	08.30.12
Operator	:	V. Goncalves

Limiting Impact Energy : >60 J

[illegible]

BAM FRICTION TEST
MEASUREMENT RESULTS AND INTERPRETATION
FOR
CELLULOSE NITRATE HERITAGE FILM

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

SENSITIVITY TO FRICTION TEST

UN Test 3 (b) (i)

BAM FRICTION TEST

Test Method

This test is carried out according to the procedure described in the following document:

1. Recommendations on the Transport of Dangerous Goods - Tests and Criteria; UN New York.

Purpose

The purpose of this test is to assess the sensitivity of a material to frictional forces.

Method

The sample is normally tested as received after sieving (using a 0.5mm sieve). All the sample that passes through the sieve is used in the test.

The material is placed on the porcelain plate and the porcelain peg is fixed in position and the load adjusted. The plate is moved under the loaded peg and the effects observed.

Criteria and Method of Assessing the Result

A series of trials is started at a load of 360N. If an "explosion" (report, crackling, sparking, or flame) is observed, the series is continued at lower loads until decomposition or no reaction is observed. The test results are assessed on the basis of whether an "explosion" occurs in any of the six trials at a friction load and the lowest friction load at which at least "explosion" occurs in six trials.

The test result is considered positive if the lowest friction load at which one "explosion" occurs in six trials is <80N and the substance is considered too dangerous for transport in the form in which it was tested. Otherwise the test result is considered negative.

Results

The results of BAM Friction Testing for CELLULOSE NITRATE HERITAGE FILM are shown on the next page. The limiting impact energy for this sample is >360 N. These results indicate that this sample is not sensitive to ignition by friction.

BAM FRICTION TEST RESULTS

UN Test 3 (b) (i)

Sample Information

Company Name : **University of Wisconsin - Madison**
Test Powder : **CELLULOSE NITRATE HERITAGE FILM**
Ref. No. : N/A
Origin of the Sample : N/A
Size Information : Sample tested as received
Sample Description : Fine, brown powder

Test Information

Test Purpose : To determine the sensitivity of the sample to friction.
Apparatus : The BAM porcelain peg and plate Friction Apparatus.
Date of test : 08.30.12
Operator : V. Goncalves

Results

Limiting Load of Sample : >360 N

Mass (kg)	Load (N)	Test number and results (x/√)					
		1	2	3	4	5	6
8.15	360	X	X	X	X	X	X

Note: "x" denotes no reaction or decomposition (change in color)
"√" denotes an explosion (includes crackling, sparkling, inflammation)

APPENDIX

Legal Disclaimer and Liability

(a) Limitation of Liability. The test procedures and/or consulting services conducted by Chilworth Technology (the "Company") were performed under controlled laboratory conditions, which the Company considers reliable. Although the Company performed its testing services pursuant to reliable and generally accepted testing procedures in the industry, the Company does not guarantee or provide any representations or warranties with respect to Client's use, interpretation or application of the test results and/or consulting services provided by the Company. Moreover, the results of the testing procedures are based upon certain assumptions, information, documents, and procedures provided by the Customer. AS SUCH, IN NO EVENT AND UNDER NO CIRCUMSTANCE SHALL THE COMPANY BE LIABLE FOR SPECIAL, INDIRECT, PUNITIVE OR CONSEQUENTIAL DAMAGES OF ANY NATURE WHATSOEVER, INCLUDING WITHOUT LIMITATION, ANY LOST REVENUE OR PROFITS OF THE CUSTOMER OR ITS CUSTOMERS, AGENTS AND DISTRIBUTORS, RESULTING FROM, ARISING OUT OF OR IN CONNECTION WITH, THE SERVICES PROVIDED BY THE COMPANY OR THE RESULTS OF ANY TESTS PERFORMED BY THE COMPANY. The Customer agrees that the Company shall have no liability for damages, which may result from Client's use, interpretation or application of the test results and/or consulting services provided by the Company.

(b) The Company's pricing of the testing services provided does not contemplate that the Company shall have any liability resulting from its performance of the testing procedures, except as otherwise set forth in the Quotation from the Company. Accordingly, the Customer shall indemnify and hold harmless the Company, its shareholders, directors, officers, employees and agents (the "*Indemnified Parties*") from and against any and all loss, cost, liability and expense, including reasonable attorney's fees and costs, which any of the Indemnified Parties may incur, sustain or be subject to, as a result of any claim, demand, action, investigation or proceeding arising out of or relating to either: (a) the testing services provided by the Company; or (b) any material, equipment, specifications or safety information (or lack thereof) supplied to the Company (or which should have been supplied to the Company) by Customer and/or any failure of such materials, equipment, specifications and safety information to comply with any federal, state or local law or safety standard.

(c) For additional terms and conditions, which apply with respect to the provision of this report, see the Quotation provided by the Company and executed by Customer. If any terms set forth in the Quotation conflict with the terms set forth herein, the terms set forth herein shall apply.



Client University of Wisconsin - Madison
Contact Mahesh K. Mahanthappa, Ph.D.
Report issue date July 11, 2014
Report number UN15219RP

SAMPLE #1, SAMPLE #2 AND SAMPLE #3

Explosion Testing

Reviewed By

Victoria Goncalves
Laboratory Supervisor

Approved By

Don B. Churchwell
Laboratory Manager

Quote / Job Numbers: 22775 / 15219
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Report prepared by S. Smith

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INTRODUCTION

This report presents the results of dust explosibility measurements performed on your **SAMPLE #1, SAMPLE #2 AND SAMPLE #3**. The results are summarized in Table 1 on the following page. The report includes a description of the test procedures and an interpretation of the results.

Chilworth Technology is experienced in providing specific advice in the areas of dust explosion prevention and control, electrostatics, thermal stability and chemical reaction hazards. Site visits to discuss operational safety or to perform plant inspection and measurements can be arranged.

Name and address of client:

Mahesh K. Mahanthappa, Ph.D.
University of Wisconsin – Madison
Department of Chemistry
1101 University Avenue
Madison, WI 53706-1322

TABLE 1

SUMMARY OF TEST RESULTS

For Test Sample: **SAMPLE #1, SAMPLE #2 AND SAMPLE #3**

Sample Name	BAM Fallhammer (J)	BAM Friction (N)
a) Sample #1	>60	>360
b) Sample #2	>60	>360
c) Sample #3	>60	>360

Note: The results given in this report apply to the sample tested. Changes in composition, particle size, and moisture content may affect the results.

**BAM FALLHAMMER TEST
MEASUREMENT RESULTS AND INTERPRETATION
FOR
SAMPLE #1, SAMPLE #2 AND SAMPLE #3**

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

BAM FALLHAMMER TEST

UN Test 3 (b) (ii)

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The sample substance being tested is enclosed in a sample cell consisting of two co-axial steel cylinders, one above the other in a hollow cylindrical steel guide ring. The cylinders are steel rollers from roller bearings with polished surfaces and rounded edges. The sample cell is placed on the intermediate anvil and centered.

Test Procedure

Chilworth Technology performs BAM Fallhammer Testing in accordance with the United Nations' (UN) Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.2 - 9/95). Substances are usually tested as received. Wetted substances are tested with the minimum content of wetting agent provided for transport.

A sample is taken with a scoop of 40 mm³. The substance is then placed in the open sample cell, which is already in the locating ring on the intermediate anvil. The upper steel cylinder is then set to be 1 mm above the lower cylinder and is held in that position by means of an O-ring.

When the sample cell is properly positioned, the dropweight is released and the impact result is observed. Distinction is made between "no reaction", "decomposition" (change of color), and "explosion" (crackling, sparkling, or inflammation).

The series of trials is started with a single trial at 10 J. If an "explosion" is observed, the series is continued with trials for decreasing impact energies until a "decomposition" result or "no reaction" result is observed. If however, a "decomposition" result or "no reaction" result is observed at 10 J, the weight is slowly increased until an "explosion" result is observed or the maximum impact energy is reached (60 J).

The limiting impact energy for a substance, is defined as the lowest energy for which an "explosion" result is obtained from at least one out of the six trials. The UN Recommendations indicate that a substance is too sensitive for transport if it exhibits a limiting impact energy of 2 J or less.

Results

The results of BAM Fallhammer Testing for these samples are shown in the following Tables. These results indicate that these samples are not particularly sensitive to ignition by mechanical impact.

Sample Information

Company Name	:	University of Wisconsin - Madison
Test Powder	:	SAMPLE #1
Ref. No.	:	N/A
Origin of the Sample	:	N/A
Size Information	:	Sample tested mixed
Sample Description	:	Coarse, orange powder

Test Purpose	:	To determine the limiting impact energy of the sample.
Apparatus type	:	BAM Fallhammer Apparatus
Date of test	:	06.18.14
Operator	:	M. Saparito

Limiting Impact Energy: >60 J

[illegible]

BAM FALLHAMMER TEST RESULTS

UN Test 3 (b) (ii)

Sample B: Sample #2

Sample Information

Company Name : **University of Wisconsin - Madison**
 Test Powder : **SAMPLE #2**
 Ref. No. : N/A
 Origin of the Sample : N/A
 Size Information : Sample tested mixed
 Sample Description : Coarse, orange powder

Test Information

Test Purpose	:	To determine the limiting impact energy of the sample.
Apparatus type	:	BAM Fallhammer Apparatus
Date of test	:	06.26.14
Operator	:	M. Saparito

Results

Limiting Impact Energy: >60 J

[illegible]

BAM FALLHAMMER TEST RESULTS

UN Test 3 (b) (ii)

Sample C: Sample #3

Sample Information

Company Name	:	University of Wisconsin - Madison
Test Powder	:	SAMPLE #3
Ref. No.	:	N/A
Origin of the Sample	:	N/A
Size Information	:	Sample tested mixed
Sample Description	:	Coarse, orange powder

Test Information

Test Purpose	:	To determine the limiting impact energy of the sample.
Apparatus type	:	BAM Fallhammer Apparatus
Date of test	:	06.26.14
Operator	:	M. Saparito

Results

Limiting Impact Energy: >60 J

[illegible]

**BAM FRICTION TEST
MEASUREMENT RESULTS AND INTERPRETATION
FOR
SAMPLE #1, SAMPLE #2 AND SAMPLE #3**

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

SENSITIVITY TO FRICTION TEST

UN Test 3 (b) (i)

BAM FRICTION TEST

Test Method

This test is carried out according to the procedure described in the following document:

1. Recommendations on the Transport of Dangerous Goods - Tests and Criteria; UN New York.

Purpose

The purpose of this test is to assess the sensitivity of a material to frictional forces.

Method

The sample is normally tested as received after sieving (using a 0.5mm sieve). All the sample that passes through the sieve is used in the test.

The material is placed on the porcelain plate and the porcelain peg is fixed in position and the load adjusted. The plate is moved under the loaded peg and the effects observed.

Criteria and Method of Assessing the Result

A series of trials is started at a load of 360N. If an "explosion" (report, crackling, sparking, or flame) is observed, the series is continued at lower loads until decomposition or no reaction is observed. The test results are assessed on the basis of whether an "explosion" occurs in any of the six trials at a friction load and the lowest friction load at which at least "explosion" occurs in six trials.

The test result is considered positive if the lowest friction load at which one "explosion" occurs in six trials is <80N and the substance is considered too dangerous for transport in the form in which it was tested. Otherwise the test result is considered negative.

Results

The results of BAM Friction Testing for these sample are shown on the next page. These results indicate that these samples are not sensitive to ignition by friction.

BAM FRICTION TEST RESULTS

UN Test 3 (b) (i)

Sample A: Sample #1

Sample Information

Company Name : University of Wisconsin - Madison
Test Powder : SAMPLE #1
Ref. No. : N/A
Origin of the Sample : N/A
Size Information : Sample tested mixed
Sample Description : Coarse, orange powder

Test Information

Test Purpose : To determine the sensitivity of the sample to friction.
Apparatus : The BAM porcelain peg and plate Friction Apparatus.
Date of test : 06.18.14
Operator : M. Saparito

Results

Limiting Load of Sample : >360 N

Mass (kg)	Load (N)	Test number and results (x/√)					
		1	2	3	4	5	6
8.15	360	X	X	X	X	X	X

Note: "x" denotes no reaction or decomposition (change in color)
"√" denotes an explosion (includes crackling, sparkling, inflammation)

BAM FRICTION TEST RESULTS

UN Test 3 (b) (i)

Sample B: Sample #2

Sample Information

Company Name : University of Wisconsin - Madison
Test Powder : SAMPLE #2
Ref. No. : N/A
Origin of the Sample : N/A
Size Information : Sample tested mixed
Sample Description : Coarse, orange powder

Test Information

Test Purpose : To determine the sensitivity of the sample to friction.
Apparatus : The BAM porcelain peg and plate Friction Apparatus.
Date of test : 06.26.14
Operator : M. Saparito

Results

Limiting Load of Sample : >360 N

Mass (kg)	Load (N)	Test number and results (x/√)					
		1	2	3	4	5	6
8.15	360	X	X	X	X	X	X

Note: "x" denotes no reaction or decomposition (change in color)
"√" denotes an explosion (includes crackling, sparkling, inflammation)

BAM FRICTION TEST RESULTS

UN Test 3 (b) (i)

Sample C: Sample #3

Sample Information

Company Name : University of Wisconsin - Madison
Test Powder : SAMPLE #3
Ref. No. : N/A
Origin of the Sample : N/A
Size Information : Sample tested mixed
Sample Description : Coarse, orange powder

Test Information

Test Purpose : To determine the sensitivity of the sample to friction.
Apparatus : The BAM porcelain peg and plate Friction Apparatus.
Date of test : 06.26.14
Operator : M. Saparito

Results

Limiting Load of Sample : >360 N

Mass (kg)	Load (N)	Test number and results (x/√)					
		1	2	3	4	5	6
8.15	360	X	X	X	X	X	X

Note: "x" denotes no reaction or decomposition (change in color)
"√" denotes an explosion (includes crackling, sparkling, inflammation)

APPENDIX

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(a) Limitation of Liability. The test procedures and/or consulting services conducted by Chilworth Technology (the "Company") were performed under controlled laboratory conditions, which the Company considers reliable. Although the Company performed its testing services pursuant to reliable and generally accepted testing procedures in the industry, the Company does not guarantee or provide any representations or warranties with respect to Client's use, interpretation or application of the test results and/or consulting services provided by the Company. Moreover, the results of the testing procedures are based upon certain assumptions, information, documents, and procedures provided by the Customer. AS SUCH, IN NO EVENT AND UNDER NO CIRCUMSTANCE SHALL THE COMPANY BE LIABLE FOR SPECIAL, INDIRECT, PUNITIVE OR CONSEQUENTIAL DAMAGES OF ANY NATURE WHATSOEVER, INCLUDING WITHOUT LIMITATION, ANY LOST REVENUE OR PROFITS OF THE CUSTOMER OR ITS CUSTOMERS, AGENTS AND DISTRIBUTORS, RESULTING FROM, ARISING OUT OF OR IN CONNECTION WITH, THE SERVICES PROVIDED BY THE COMPANY OR THE RESULTS OF ANY TESTS PERFORMED BY THE COMPANY. The Customer agrees that the Company shall have no liability for damages, which may result from Client's use, interpretation or application of the test results and/or consulting services provided by the Company.

(b) The Company's pricing of the testing services provided does not contemplate that the Company shall have any liability resulting from its performance of the testing procedures, except as otherwise set forth in the Quotation from the Company. Accordingly, the Customer shall indemnify and hold harmless the Company, its shareholders, directors, officers, employees and agents (the "*Indemnified Parties*") from and against any and all loss, cost, liability and expense, including reasonable attorney's fees and costs, which any of the Indemnified Parties may incur, sustain or be subject to, as a result of any claim, demand, action, investigation or proceeding arising out of or relating to either: (a) the testing services provided by the Company; or (b) any material, equipment, specifications or safety information (or lack thereof) supplied to the Company (or which should have been supplied to the Company) by Customer and/or any failure of such materials, equipment, specifications and safety information to comply with any federal, state or local law or safety standard.

(c) For additional terms and conditions, which apply with respect to the provision of this report, see the Quotation provided by the Company and executed by Customer. If any terms set forth in the Quotation conflict with the terms set forth herein, the terms set forth herein shall apply.

Appendix 5: Additional Initiatives

1. Annotated bibliography keywords
2. Sample annotated bibliography entries
3. Oral history interview questions
4. Unedited transcript of interview with Ken Weissman

Classify all articles with the following 2 designations:

Source Community:

1. Archivists
2. Conservators
3. Chemists and Polymer Scientists
4. Historians (film historians and chemistry/polymer science historians)
5. Film Industry Practitioners
 - a. Film Stock Manufacturers
 - b. Lab Technicians
 - c. Projectionists/Theater Managers
6. Safety or Standards Organizations
7. Government Agencies
8. General Public

Source type:

1. Peer reviewed or academic article
2. Historical overview/account
3. Literature review
4. Anecdote
5. Popular Press article
6. Email or forum posting
7. Website
8. Conference proceedings
9. Trade article
10. Practitioner handbook
11. Safety standards
12. Government Publication

Classify articles with following designations as applicable:

Type of cellulose nitrate:

1. Pyroxylin
2. Xylonite/Ivoride/Parkesine
3. Collodion
4. Cellulose nitrate film stock
 - a. Moving image film
 - b. Sheet film
 - c. X-Ray film
5. Cellulose nitrate object
6. Cellulose nitrate adhesive
7. Cellulose nitrate lacquer
8. Cellulose nitrate spray paint

Nitration Level:

1. Mention/discussion of nitration level

2. Connection between nitration level and flammability
3. Connection between nitration level and decomposition

Plasticizers:

1. Type of plasticizer
 - a. Camphor
 - b. Phthalate
 - c. Phosphate ester
 - d. Other (glycerol, castor oil)
2. Plasticizers and flammability
3. Loss of plasticizer
4. Retention of plasticizer

Film Processing/Handling:

1. Production of film stock
2. Development
 - a. Metol (Elon, Rhodol)
 - b. Borax
 - c. Edinol
 - d. Glycin
 - e. Hydroquinone
 - f. Ortol
 - g. Phenidone
 - h. Pyro
 - i. Rodinal
 - j. Serchol
3. Hardeners
4. Stop Bath
 - a. Chromium potassium sulfate (chrome alum)
 - b. Potassium alum
5. Fixing
 - a. Sodium thiosulfite ("Hypo")
 - b. Ammonium thiosulfate
 - c. Borax
 - d. Glycerin
6. Washing
7. Drying
8. Post-development treatment
 - a. Glycerin bath
 - b. Waxing
 - c. Lacquering
 - d. Waterproofing
 - e. Cleaning
9. Sepia Toning
10. Tinting/toning color process
11. Metallic Toning process

12. Damage to film during processing
13. Damage to film during use

Film Fires

1. Unspecified/minor fires
2. Bazar de la Charite Fair, Paris, 1897
3. Market Place, Bilston, Stafford, UK, 1898
4. Ferguson Building, Pittsburgh PA, 1909
5. Thanouser, New Rochelle NY, 1913
6. Lubinville Studio, Philadelphia PA, 1914
7. Edison Factory, West Orange NJ, 1914
8. Inceville, Santa Monica CA, 1916
9. *SS Duilio*, Atlantic Ocean, 1928
10. Cleveland Clinic, Cleveland OH, 1929
11. Consolidated Film Industries, Hollywood CA, 1929
12. Glen Cinema, Paisley, Scotland, UK, 1929
13. Basement Laboratory, Salt Lake City, UT, 1929
14. University of California Hospital, San Francisco CA, 1930
15. Esmeralda Theater, Talcahuano, Chile, 1932
16. Warner Bros. Studio, Burbank CA 1934
17. Fox Film Corp, Little Ferry NJ, 1937
18. New York/New Jersey Area, 1949
19. Cinematheque Francaise, Paris, 1959
20. National Film Board of Canada, Beaconsfield, Quebec, 1967
21. National Archives, Suitland, MD, 1977
22. George Eastman House, Rochester NY, 1978
23. National Archives, Suitland, MD, 1978
24. Cinematheque Francaise, Le Pontel, Villiers Saint-Frederic, 1980
25. New York Historical Society, New York City, 2003

Chemical Study Parameters:

1. CN sample recast
2. CN sample tested intact
3. CN sample produced for study
4. Emulsion removed
5. Emulsion intact
6. Plasticizer removed
7. Plasticizer included
8. Film sample “stabilized” with something like Tris-stuff
9. Non-film CN product studied
10. Acetate film studied

Analytical Techniques Used:

1. Fluorescence
2. X-Ray fluorescence spectroscopy
3. Gas Chromatography

4. Aqueous Extraction
5. Aqueous Extract of Emulsion
6. Emulsion flow/melting point
7. Molecular Weight
8. Solubility of Base
9. Mechanical/Tensile Strength
10. Scratch resistance / scratch testing
11. pH Changes
12. IR or FTIR
13. UV or UV-Vis
14. Colorimetry
15. NMR (Nuclear Magnetic Resonance)
16. Thermomechanical Analysis
17. TGA (Thermogravimetric Analysis)
18. Gravimetric analysis
19. Dynamic Mechanical Analysis
20. Accelerated Aging
21. Ion Chromatography
22. Gel permeation chromatography
23. Elemental Analysis or Combustion Analysis
24. ICP (Inductively Coupled Plasma Spectroscopy)
25. AA (Atomic Absorption) or AE (Atomic Emission) Spectroscopy
26. Profilometry
27. Optical Densitometry
28. XPS (X-ray Photoelectron Spectroscopy) or Auger Spectroscopy
29. Density of Image Measured
30. Visual Examination
31. Microscopy (light, optical, polarized light, etc.)
32. X-Ray Diffraction
33. Viscometry
34. Testing for Residual Hypo (mercuric chloride)
35. Ashing

Mechanisms for decomposition:

1. O-N cleavage or nitrate ester hydrolysis
2. Chain scission (chain breaking at the C-O-C bonds)
3. Ring disintegration
4. Autocatalytic
5. Reactions involving NO, NO₂ or HNO₃
6. Secondary decomposition involving UV
7. Underlying cause unknown

Variables affecting decomposition:

1. Acids
2. Alkalis
3. Temperature

4. Relative humidity
5. Light
6. Age
7. Storage containers
 - a. Iron catalyzes decomposition
 - b. Vented
 - c. Not vented
8. Physical damage
 - a. Abrasion
 - b. Overuse
 - c. Changes in sorption behavior
 - d. Biological degradation (mold or bacterial growth)
9. Product manufacturing
 - a. Inadequate removal of sulfuric acid
 - b. Inadequate removal of hypo
 - c. Addition of basic stabilizers
 - d. Addition of other stabilizers (neutral, antioxidants, etc.)
 - e. Presence of dyes or fillers
10. Interactions between emulsion and base
 - a. Physical integrity of emulsion
 - b. Image density
 - c. Gelatin
 - d. Base decay as primary trigger
 - e. Emulsion as primary trigger
 - f. Emulsion and abrasion

Variables affecting combustibility

1. Decomposition
 - a. Direct correlation
 - i. Linear
 - ii. Non-linear
 - b. Inverse correlation
 - i. Linear
 - ii. Non-linear
2. Nitration level
 - a. Direct correlation
 - b. Inverse correlation
3. Relative Humidity
 - a. Direct correlation
 - b. Inverse correlation
4. Temperature

Brown powder stage

1. Most dangerous
2. Shock-sensitive
3. Inert

Release of Gases

1. Build up of gases creates explosion hazard
2. Trapped gases catalyze decomposition
3. Effect of heat on production of gases
4. Respiratory hazard
5. Composition of gases
6. Explosive nature of gases generally

Public relations

1. Emphasizes risk
2. Deemphasizes risk

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Accelerated aging to study the degradation of cellulose nitrate museum artefacts

Submitted by siteadmin on Thu, 08/07/2014 - 12:11

Title	Accelerated aging to study the degradation of cellulose nitrate museum artefacts
Publication Type	Journal Article
Year of Publication	2011
Authors	Quye A, Littlejohn D, Pethrick RA, Stewart RA
Journal	Polymer Degradation and Stability
Volume	96
Pagination	1934-1939
Keywords	Analytical Techniques used: Accelerated aging, Analytical Techniques Used: Aqueous Extraction, Analytical Techniques Used: Elemental Analysis or Combustion Analysis, Analytical Techniques Used: Gel Permeation Chromatography, Analytical Techniques Used: Ion Chromatography, Analytical Techniques Used: IR or FTIR, Analytical Techniques Used: Molecular Weight, Chemical Study Parameters: CN sample produced for study, Chemical Study Parameters: Non-film CN product studied, Mechanisms for decomposition: Autocatalytic, Mechanisms for decomposition: Chain scission, Mechanisms for decomposition: O-N cleavage or nitrate ester hydrolysis, Nitration Level: Mention/discussion of nitration level, Plasticizers: Loss of plasticizer, Plasticizers: Type of plasticizer - Camphor, Source Community: Chemists & Polymer Scientists, Source Community: Conservators, Type of Cellulose Nitrate: Cellulose Nitrate Object, Variables Affecting Decomposition: Product manufacturing - Inadequate removal of sulfuric acid
Abstract	Cellulose nitrate is susceptible to hydrolysis as well as loss of plasticiser when left in a humid atmosphere. A comparison of the ageing behaviour of cellulose nitrate samples prepared from cotton linters was used to simulate the artefacts studied in a previous study. Certain artefacts were also subjected to accelerated ageing at 12%, 55% and 75% relative humidity at 70 degrees C. The rate of degradation was observed to vary with the RH, indicating the connection between the absorption of moisture and the hydrolysis process. The effect of varying the sulphate level on the rate of hydrolysis was studied using <.01mg g-1, 2 mg g-1 and 5 mg g-1 of sulphate and distinct differences were observed which is consistent with the conclusions drawn for a study of a number of artefacts. The observed rates of degradation are consistent with previous studies on cellulose nitrate. The degradation was studied using a combination of infrared spectroscopy, ion chromatography and gel permeation chromatography. The analysis was complemented by a study of the weight changes which occur during ageing.
Notes	Studies were undertaken on films and disks of cellulose nitrate made for the experiment with different elemental make-ups and on archival cellulose nitrate objects. Article is significant for its focus on the roles played by sulphate, zinc, fillers and the thickness of the sample on the rate of decomposition. No discussion is given about cellulose nitrate's flammability.

[Google Scholar](#)

The Nature of the Degradation of Archival Cellulose-Ester Base Motion-Picture Film: the Case for Stabilization

Submitted by siteadmin on Thu, 08/07/2014 - 12:11

Title	The Nature of the Degradation of Archival Cellulose-Ester Base Motion-Picture Film: the Case for Stabilization
Publication Type	Journal Article
Year of Publication	1988
Authors	Allen N.S., Appleyard J.H., Edge M., Francis D., Horie C.V., Jewitt T.S.
Journal	The Journal of Photographic Science
Volume	36
Pagination	34-39
Keywords	Analytical Techniques used: Accelerated aging, Analytical Techniques used: Emulsion flow/melting point, Analytical Techniques Used: IR or FTIR, Analytical Techniques Used: pH changes, Analytical Techniques Used: UV or UV-Vis, Analytical Techniques Used: Viscometry, Chemical Study Parameters: Acetate film studied, Chemical Study Parameters: CN sample produced for study, Chemical Study Parameters: Emulsion removed, Mechanisms for decomposition: O-N cleavage or nitrate ester hydrolysis, Mechanisms for Decomposition: Underlying cause unknown, Type of Cellulose Nitrate: Cellulose Nitrate Film Stock - Moving image film, Variables affecting decomposition: Acids, Variables Affecting Decomposition: Relative humidity, Variables affecting decomposition: Temperature
Abstract	The degradation of a number of cellulose acetate/nitrate based 35mm cinematograph films has been studied by moisture regain, uv absorption, viscometry, pH and degree of insolubilization. Analysis of naturally aged films indicates a correlation between moisture regain, acidity and degree of degradation. Artificial ageing studies at various temperatures and at different humidities show that temperature, moisture regain, and pH are important related factors in the degradation mechanism. The results show conclusively that the degradation of ester based film is associated with an acid catalysed hydrolysis of the ester group resulting in a consequent reduction in the molecular weight of the polymer. It is also indicated that there is a minimum concentration of acid necessary to produce hydrolysis and that above this threshold the less moisture present in the environment the more rapid the rate of degradation. The results therefore call into question current standards for storage of ester base motion-picture films and suggest stabilization as an alternative means of preservation
Notes	This article's various tests add support for a number of the proposed contributing factors to nitrate decomposition, principally ester hydrolysis and its connection to molecular weight. It also makes arguments about the nature of the hydrolysis preceding decomposition and the potential for stabilization. Our own studies have not confirmed the correlation between nitrate decomposition and molecular weight.

The Preservation of Motion Picture Film

Submitted by siteadmin on Thu, 08/07/2014 - 12:11

Title	The Preservation of Motion Picture Film
Publication Type	Journal Article
Year of Publication	1967
Authors	Calhoun JM
Journal	The American Archivist
Volume	30
Pagination	517-525
Keywords	Film Processing/Handling: Development, Film Processing/Handling: Drying, Film Processing/Handling: Fixing, Film Processing/Handling: Post-development treatment - Cleaning, Film Processing/Handling: Post-development treatment - Lacquering, Film Processing/Handling: Post-development treatment - Waterproofing, Film Processing/Handling: Washing, Source Community: Archivists, Source Community: Conservators, Type of Cellulose Nitrate: Cellulose Nitrate Film Stock - Moving image film, Variables affecting decomposition: Physical damage, Variables Affecting Decomposition: Physical damage - Biological degradation (mold or bacterial growth), Variables Affecting Decomposition: Product manufacturing - Inadequate removal of hypo, Variables Affecting Decomposition: Relative humidity, Variables Affecting Decomposition: Storage containers - Not vented, Variables affecting decomposition: Temperature
Abstract	This paper is primarily a review of information developed over a period of years, based on both laboratory experiments and practical experience, to provide the best possible guides for preserving motion-picture films. Different types of film base and both black-and-white and color motion-picture films will be discussed from the standpoint of their processing, handling, and storage. Color films are included in the discussion because the preservation of dye images is also desired, even though these are not normally considered archival material.
Notes	This paper reviews standard practices for handling motion picture films in preservation. It includes much attention to factors that contribute to deterioration such as fungal growth and poor development. It adheres to the five stage model of nitrate decomposition.

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The Inflammable Picture Film

Submitted by siteadmin on Thu, 08/07/2014 - 12:11

Title	The Inflammable Picture Film
Publication Type	Journal Article
Year of Publication	1922
Corporate Authors	Association NFire Prote
Journal	Quarterly of the National Fire Protection Association
Volume	16
Pagination	109-110
Keywords	Public relations: Emphasizes risk, Source Community: Safety or Standards Organization, Type of Cellulose Nitrate: Cellulose Nitrate Film Stock - Moving image film
Abstract	Account of various resolutions passed to attempt to outlaw cellulose nitrate film, given the ability to substitute acetate stock. Follows from ordinance passed in Paris to phase out the display nitrate by January 1925.
Notes	Article points toward the desire of safety organizations - namely fire fighters - to eliminate cellulose nitrate film stock because of the burden it places on inspectors. The resolutions passed emphasize the danger of cellulose nitrate and urge the film industry to fully adopt cellulose acetate film stock.

[Google Scholar](#)

Oral History Questions

Conservators

1. Would you tell me a bit about your career and what you do?
2. How did you first start working with nitrate film?
3. How did you learn about the dangers of nitrate film?
4. How did you learn about the safety regulations and best practices governing nitrate? Have any safety regulations or practices changed since you first started working with nitrate?
5. What do you know about the dangerous aspects of nitrate film?
6. Can you describe any experiences you have had with toxic gas releases or fire that involved nitrate film?
7. Have you ever had to find ways to house, handle or treat deteriorating nitrate film? What sort of steps did you take and why?
8. Based on your experience, do you think that the safety regulations and best practices that currently govern nitrate film are appropriate and effective? Are there particular regulations or practices that you have found to be especially useful or not useful?
9. Are there particular methods or practices that you have used when handling nitrate that deviate from those prescribed? What experiences and anecdotes are informing your practices?

Archivists

1. At what point in your career did you start working with nitrate film? Did you know anything about nitrate film before you had to start working with it?
2. How did you learn about caring for nitrate film? Were there training sessions? Classes?
3. How has the approach of caring for and regulating nitrate changed since you started working with nitrate film?
4. Have you ever experienced an emergency such as a nitrate fire or noxious gases?
5. What challenges have you faced in managing and/or planning a facility used/built for storing nitrate film? What challenges are there to moving a large collection of nitrate film?
6. Based on your experience, do you think nitrate film is regulated and handled properly? Are there changes you would like to see – i.e. regulations, care, education?
7. Are there things, based on your personal experience working with nitrate that you think people should know about nitrate? Do you have any stories you would be willing to share?

Lab personnel

1. Can you tell me a bit about your background – how you got into the film business, when you started working in a film lab, what drew you to this type of work?
2. How did you first start working with nitrate film, and how did you learn about the dangers of nitrate film?
3. How did you learn about the safety regulations and best practices governing nitrate? How have these regulations or practices changed since you first started working with nitrate?
4. Which regulations or practices do you find are especially important to lab work?
5. Have you ever experienced any nitrate-related disasters/scares? ?
6. In what ways, other than the safety issues, do you find nitrate film more difficult to work with than other film types, if at all?
7. Do you think that the safety regulations and best practices that currently govern nitrate film are appropriate and effective? Are there particular regulations or practices that you have found to be especially useful or not useful?
8. Are there particular methods or practices that you have used when handling nitrate that deviate from those prescribed?

Projectionists

1. Can you tell me a little about your background – how you got started as a projectionist, what drew you to this type of work, etc?
2. How did you first start working with nitrate film, and how did you learn about the dangers work working with it?
3. How did you learn about the safety regulations and best practices governing the projection of nitrate film? Have any safety regulations or practices changed since you first started projecting nitrate?
4. Have you ever had to deal with a nitrate fire or other type of nitrate disaster in the projection booth?
5. Based on your experience, do you think that the safety regulations and best practices that currently govern the projection of nitrate film are appropriate and effective? Are there particular regulations or practices that you have found to be especially useful or not useful?

Wisconsin Center for Film and Theater Research

Nitrate Motion Picture Film Oral History Interviews

Ken Weissman

INTERVIEWER: Okay. So today is Tuesday, June 16th, 2015. My name is Mary Huelsbeck, and I'm speaking with Ken Weissman of the Library of Congress. Ken is the supervisor of the film preservation laboratory for Library of Congress. So, Ken, why don't you start off by telling me a little bit about yourself and how you became an archivist.

RESPONDENT: Okay. That's fine. Okay. So I've actually worked for the Library of Congress, it will be 34 years this September, this coming September. And prior to that, I had roughly four years of post production work in various film related areas, most notably when I was in the United States Air Force, which is really how I got started in motion pictures. I was selected to work as a, what's called a continuous photo processing specialist, which is the Air Force name for people that run automated or semi-automated film developing equipment primarily.

They also do printing and things like that. But the one thing that was a bit unusual about my experience in the Air Force is that I was actually assigned to a motion picture unit. And that's, there's only a few of those that the Air Force had at the time. Or as most of my colleagues and fellow trainees were assigned to cognizant technical groups, which are, it's a totally different type of machine and specialized in wide films of relatively long length, 100' or 200' of film, but unlike a motion picture film, which can be several thousand feet in length.

But like I said, I was assigned. Actually I did a program called Swap where I was, when I was in tech school, and we were learning all about photo processing, when we got our orders for our first permanent duty assignment, I was originally scheduled to go to England at RAF Alconbury. And a classmate of mine was a native Californian, and she was assigned to go to Vandenberg Air Force Base in California. And she asked if I would swap orders with her so that she could get out of California. And I said sure, yeah. I've never been to California, so what the heck, right?

Well, it turns out that the assignment in California was actually in a motion picture group, the 1,369th audio visual squadron, which provided photographic coverage and motion picture coverage of the space launches out of Vandenberg Air Force Base. So I was, you know, totally by happenstance, got involved in motion pictures. And this is, like I said, typically post production work for myself because we developed the films and printed them, timed them or graded them, some people call it.

So that was the area in which I worked. And then my second assignment was actually on the other side of the mission, so to speak, was actually in Hawaii at Hickam Air Force Base. The space launches that occurred out of Vandenberg typically sent satellites into polar orbit. And every now and then, those satellites, especially the spy satellites would come back down. And the mission at Hickam was to catch those spy

satellites and then get the information, the data that they had collected. And once again, our unit had provided the motion picture coverage for those missions.

INTERVIEWER: Okay. And you were in the Air Force, what, from '77 to '81? Is that correct?

RESPONDENT: That's correct.

INTERVIEWER: Okay.

RESPONDENT: Now, I mean, I got, I went in in March of '77. But I actually didn't get to my first duty assignment until September or so of '77. So it was a few months later, after basic training and tech school. And then that's how I got started in motion picture work. And then when I got ready to get out of the service in '81, you know, you've got to love your mom, right? So she's scouring the newspapers for jobs that her kid might be able to do when he gets out of the service so he doesn't have to live at home. And the . . .

INTERVIEWER: She didn't want you to move back home?

RESPONDENT: Well, no. She didn't mind me moving back home. But she didn't want me to be there firmly entrenched. And it worked out just fine. But the interesting thing about that timing was that the Library of Congress was getting ready to open its newly established film preservation laboratory out at Wright Patterson Air Force Base, which is near Dayton, Ohio, which is where I was from.

So, you know, another set of happy coincidences, if you will. And like I said, the timing was just about right because she saw this ad in the Sunday paper and mailed it to me because these were well before the days of e-mail and all that other stuff and the Internet. So she mailed it to me. I got it in the mail like on a Thursday. And the applications had to be submitted by the following Monday. So I very hurriedly put it together, Fed Ex-ed it off to the Library of Congress and didn't hear anything for six months.

So got out of the service, was working in private enterprise in Dayton at a company that didn't do motion picture work but did photographic coverage and presentations for sales conferences and things like that. And then all of a sudden, I get a phone call from the gentleman who was to become my boss at the Library, asking me if I was still interested in the position, and did I want to have an interview? And I said yes and went to the interview out at Wright Pat. And a few weeks later, I was hired to be one of the people that opened up the lab at Wright Pat. And as they say, the rest is history.

INTERVIEWER: Now had you had any experience working with Nitrate before that?

RESPONDENT: I did not. The only, actually my only interaction with Nitrate film prior to that was, once again, it was at Vandenberg Air Force Base when all of a sudden, we're working one day, and all of a sudden all of the fire alarms go off. We exit the

building as we would want to do in the fire alarms. And a rumor very quickly circulated that some, quote, unquote, idiot had brought in some nitrate film to the film library. And, oh, my God, how could they bring such a dangerous substance into our building knowing it was either likely to just catch fire or explode, you know, those kinds of things.

So that was my initial experience with what was allegedly nitrate film. I presume it actually was. I didn't ever see the film. But because the unit in which I worked had a revolving library for, you know, any of the Air Force units could check out films and things like that for their own use. So somebody apparently brought a roll of nitrate film and caused the building to be evacuated. And then the bomb squad came and took it all, took it away. And so everything was cool after that. So that was, like I said, my first raw experience with nitrate film at a distance.

And of course, when I first starting working for the library, we had nitrate film all surrounding us basically. And then I learned very quickly that, A, it's not going to explode if you look at it cross-eyed. And B, it's not any more likely to catch fire even than the average piece of paper on your desk is. So there's a lot of, you know, misconceptions and panic that is associated with the word that is really kind of . . . and if you think about it, you know, it was used in the industry for the, you know, professional film making industry, for over 50 years, and hardly anybody ever died, you know.

You know, there's occasionally this story or that story about a roll catching fire, or certainly in projectors, it's a possibility. But most of the stories, if you look at them closely, most of them are apocryphal, so there's no, very little in the way of any kind of, you know, scientific evidence that's ever been gathered. But you have stories about a guy, you know, a projectionist was rewinding a roll of nitrate film in the booth, and it ignited as a result of static electricity, only to find out that the guy was actually standing there smoking as he was doing it. And probably the cause was an ember from the cigarette dropped onto the film and caused it to catch fire, but if it even caught fire, you know, you just don't know so.

INTERVIEWER: So then how did you learn about nitrate? Was it all on the job training?

RESPONDENT: Yeah. It was pretty much on the job training. We had a number of pretty experienced people that came from Washington to start up the lab in Dayton. My boss, for example, was old time film guy. He used to work for the Ansco company in Binghamton, New York, which at the time he was working for Ansco, it actually a pretty rigorous competitor of Eastman Kodak.

INTERVIEWER: And what was his name?

RESPONDENT: His name is Rudy Buchel, B-u-c-h-e-l. Unfortunately, he passed away a few years ago. So he's not available to talk to any longer. But he was our supervisor. And he and Arnie Downs, who was his probably most trusted confidant, I guess is the way to, had worked in, the library did have film lab in the, I believe it was in the basement of the Jefferson building. But when the National Archives had their fire out in Suitland, Maryland in 1977-ish, they closed the nitrate lab down for the library. In fact, they essentially banned nitrate film from being on Capitol Hill as a result of that.

The library certainly abandoned it, and I believe most other agencies did as well. So and it was because the spectacular fire that had occurred at the National Archives vaults in Suitland. And certainly, nitrate film is flammable, and it needs to be respected. And there's all kinds of ways it can catch fire, but if you, you know, in its normal handling of it, it's not going to spontaneously combust. It's not going to ignite for no reason.

There's virtually every story of a nitrate fire, if you look into it, it tells you exactly why it caught fire, because it got heated by some manner, shape or form that it shouldn't have been and/or some person did something stupid or several people did a number of things that were wrong, and that's what caused the fire. But just like most fires, you know. It's human error as much as anything else so.

But in handling the nitrate, we very quickly learned that the overreaching principle is it is film. And you need to handle it just like you do virtually any film, being aware that it is, you know, flammable. And so that's kind of always in the back of your mind. And I think most people find that if they respect it, you know, it's just fine.

You know, you think about it, your everyday life, what are you driving around in your car? You know, you generally got anywhere from 10 to 20 gallons of highly flammable and explosive gasoline right behind you. And people don't give it a second thought. But you bring a roll of nitrate film in a building, and all of a sudden, they evacuate it and call the bomb squad so anyway. A little bit of an absurd reaction.

INTERVIEWER: So how has the approach of caring for and regulating nitrate changed over the years? I mean, you know, shipping, handling, what changes have you seen over the years?

RESPONDENT: Well, the biggest changes I've seen aren't so much in the code, NFPA 40 code, although there have been some significant changes in the storage, long-term storage of nitrate film. I think probably, at least as far as archives go, probably one of the biggest things that has happened is a difference in approach as far as, for example, the library never used to ship nitrate film between the months of March and October. You know, you could only ship it during the winter. So that has changed.

Now we try not to ship, you know, in July. We certainly urge our clients to not ship during the extremely warm summer months. But it's not so much because of a fire risk, but rather more so a risk towards the content of the collections, you know, getting the film warm. And especially if it's already an aged nitrate film that, you know, has some level of deterioration within it happening. And if it warms up, then it gets warmer quicker. You know, it starts to deteriorate quicker. I misspoke there. But there have been some changes in the code.

Like I say, the most notable ones being for long-term storage vaults. You can now, there used to be a requirement that each vault had its own separate air handling system. There could be no interconnecting ductwork, anything that could help, at least in theory, a fire spread from one vault to the next. So essentially, each vault was its own self-contained building, if you will. There have been some relief in that. I believe it started with the 2001 code. It may have been the 1997 where they actually allowed you to have interconnecting ductwork as long as there were appropriate fire dampers and things like that installed.

And that's been a big change because for our facility, and for the facility out at UCLA, certainly those two, which were built after. Well, actually, ours was built, and it kind of resulted in this code change because we asked for a variance. And we did some fire damper testing and things that essentially then became adopted by the NFPA as an accepted alternative to separate air handling systems for each vault. You could have interconnecting ducts as long as you had these very robust fire dampers and appropriate levels of alarm and things that caused them to shut. So that was really helpful. Without that, it would have been a very, very difficult sell and very expensive to both make the vaults, but even more importantly, to maintain them.

If you talk with the folks at the Museum of Modern Art, and their experiences with their vaults and the fact that they essentially have to, are now going through and re-changing all of the air-handling systems in each vault, it has become a nightmare to maintain for them. So I believe that, I don't think, I think Eastman house vaults were built under that code as well so. But that I'm not absolutely certain of. But it's, you know, it's a, that's really been I think probably the main change that I can think of.

There have been some changes in shipping regulations that allow you to essentially ship nitrate film in a cardboard box as long as it's a DOT approved shipping container. And those have to meet certain certifications for burst testing and things like that so that if a box is dropped, you know, all the film won't fall out of it, roll out all over the place and cause a problem. So, you know, there have been some changes like that. But I would say the most significant one was the long-term storage in the common area and like systems that you can now have, making it really possible to build a modern vault that can be used for nitrate film.

INTERVIEWER: Okay. And what about disposal, have regulations or the way you dispose of nitrate film changed?

RESPONDENT: Not significantly that I can think of. I mean, you still have to, you know, put it under water while, deteriorated film has to be put under water while it's awaiting disposal. And then, I believe what eventually happens, it's typically incinerated, but it can go to a landfill as well. So I think, and I don't think that's changed. I think, I don't recall any changes in that since I've been particularly aware of the NFPA 40 nuances. But I could be wrong on that too so.

INTERVIEWER: Okay.

RESPONDENT: If someone says differently, I'm perfectly willing to consider that as a possibility.

INTERVIEWER: Okay. Have you ever experienced an emergency with nitrate such as a fire or a buildup of gases.

RESPONDENT: No. I haven't. And in fact, one of the requirements for building on nitrate storage facilities, I find really kind of silly, especially for certain applications. Okay. So Let's say you have a building that has a number of vaults. And then there is a, each vault, of course, is required to be fully sealable and closed off, and can now

have common ducting as we've already talked about. But there may be a hallway, of course, that allows you to go from, grant you access to the vault, a central corridor, if you will. It's required that each of those, any electrical fixtures within that corridor, which would include lights and light switches and things like that, meet Class 1 Division II explosion protocols.

And I just find that ridiculous because the typical off gassing that nitrate film does is not flammable at all. What those are really designed for is to prevent, if fumes from a fire get into the hallway, then in theory, if someone would then turn a light on or off, there could be an arcing in the switch, which could then cause those gases to explode. And that's theoretically possible. But if the nitrate vaults are built to the spec that the nitrate vaults are required to be built, that can happen because those gases will not get into the hallway.

So, you know, it's, and I've actually seen facilities where the interpretation by the authority having, the local authority having jurisdiction, which is typically the fire marshal of the locality, you know, where the vaults are located. You know, they interpret that differently. So it's, you know, some people, I've been in nitrate vaults where there are no things in the corridors.

But our local authority said that all of our systems had to meet these Class 1 Division II explosion standards which resulted in actually as a practical matter, resulted in us not being able to bring nitrate film in for about six months while they changed the strobes for the, you know, the visual part of the fire alarm system. You know, because some people are deaf, ADA requires them to have a visible strobe right?

INTERVIEWER: Right.

RESPONDENT: And those strobes could not, were not and did not meet Class 1 Division II standards. They actually had to engineer and build strobes that did and then install those. And that took about six months before that occurred. You know, so I just found it weird that, you know, that was even such an issue. But it was. So who am I to question?

INTERVIEWER: Now being a federal facility, is there any conflict between the federal regulations and the local regulations?

RESPONDENT: Not, I wouldn't say that. We are a federal facility 100%, absolutely. We're on federal land. The management of the facility is not done by our agency but rather another federal agency called Architect of the Capitol. And most of the discrepancies, and for lack of a better term, pissing contests that occur, are as a result of, you know, that one federal agency versus another federal agency, and their fire marshals versus our fire marshal.

And everybody is saying that, oh, no, that's my property and not necessarily agreeing on approach. We had that at Wright Patterson too where the Air Force, we were on Air Force property there and an Air Force owned building, Air Force supply, and the library paid rent essentially. And yet the library tried to exert its influence. The Air Force, for the most part, wouldn't have any of it. But it put me in a rather awkward position at times . . .

INTERVIEWER: Sure. Yeah.

RESPONDENT: . . . trying to manage the situation. But, you know, for the, I don't know that we've ever had a problem with a local authority. You know, the county or city, that's here in Culpepper, nor did we have any issues that I'm aware of out at Wright Pat. Although Wright Pat had pretty much staked a claim in the towns and county that surrounded Wright Pat or that Wright Pat was actually located in, absolutely acquiesced to the Air Force and said, yeah, that's your property, you know, you run it by your rules.

And if something comes off of your property and causes us a problem, then we're going to have words. But and that occasionally did happen. But for the most part, the Air Force is actually really sensitive to the locals. And unless it was something that involved a national security issue that they felt strongly about they pretty much followed the local rules. And the same here, our architect to the Capitol landlords are actually very, very attuned to the local authorities and will bend over backwards, in fact, to the point sometimes where I say, you know what? Every now and then, you've got to rattle the big federal stick and say, we're going to do it this way anyway.

Because it's not really an issue. You know, if it's really, truly a safety or a safety hazard or a pollution hazard or something like that, there's absolutely never any question. We follow the rules. But, you know, occasionally there are really things that don't matter. And it's more a matter of policy, and acquiescing to their wishes in those cases seems to be a mistake. And we don't do it too often, but we have in the past. Anyway, that's more of a political thing where they don't want bad press. They don't want an article in the paper saying, oh, look what the feds are doing up on Mount . . . you know, that kind of thing.

INTERVIEWER: Keep everybody happy.

RESPONDENT: Yeah. Exactly.

INTERVIEWER: So how big is the Library of Congress nitrate collection?

RESPONDENT: We estimate it at somewhere between 130 and 140 million feet. That's our official estimate. I don't think it's quite that large. But it's probably approaching that.

INTERVIEWER: Okay. And was all of that at Wright Patterson?

RESPONDENT: Most of it was. Well, actually, yeah. In the latter years of Wright Pat, it was all at Wright Pat. Because they did close the Suitland vaults down and moved everything out to Wright Pat at some point. So it was all at Wright Pat, and it was all moved here. Now we've acquired additional nitrates since we've gotten here, but everything that was at Wright Pat was moved here.

INTERVIEWER: Okay. So you talked a little bit before about shipping. Could you talk a little bit about shipping of mass quantity of nitrates to the new facility?

RESPONDENT: Yeah. That was a really, really interesting exercise. It's really a challenging logistics problem because the goal was, we had our collection computerized at Wright Pat. We actually, prior to moving it, went through and essentially replaced all of the cans that needed to be replacing and had everything bar coded prior to the move. But even with that, when the Wright Pats were originally loaded, which, of course, was late '60s, early '70s, well before any kind of computer inventory systems were typically available, everything was loaded in such a fashion so that if we didn't know specifically where a roll of film was, we could generally have a good idea because all of the Columbia stuff was in a series of vaults.

All of the Universal was in another series. All of the Warner Brothers, etc., and then it started off with all original camera materials. And then we had fine grains in another series of vaults. So, you know, we had it organized by various categories that allowed us to, even if we didn't know specifically in a vault, let's say, of course, all this was on a file card system. So a file card would say that, you know, *Mr. Smith Goes to Washington* was in Vault 39 Section 2, Shelf 3 through 5, for example. And those numbers are just off the top of my head.

But we had it categorized down to that level so we could pretty much walk, you know, pull out the catalog card and know exactly where it was in the vaults and go find it. Or sometimes the catalog cards got misplaced or misfiled or just got lost, or the information on them wasn't current because something got moved. And but we could still, you know, narrow it down to a certain range of vaults and usually within shelves in that vault and find it.

So what we wanted to do, when we were getting ready to move the collection out of Wright Pat over here to Culpepper, is maintain that at least to some degree. You know, because there's, you know, every now and then, your computer is not on, or you don't have access to your online databases. And we still wanted to be, if necessary, if for whatever reason we lost our databases for more than a few minutes, and we absolutely positively needed to be able to find something, we wanted to be able to do it.

So we designed a moving protocol that basically unloaded the shelves at Wright Pat in more or less the same order and then reloaded those shelves here in Culpepper so that things pretty much replicated the order in the way they were in Dayton. Now, of course, everything is in a computer database. We know each cubicle is bar-coded. Each role of film is bar-coded. As long as we have access to our database, we can find, we know exactly where it is.

INTERVIEWER: Right.

RESPONDENT: But if the, you know, if we were to have, you know, a mass power outage that lasted for hours or days even and for whatever reason, or just, you know, some kind of, Library of Congress got hacked like OPM did, and we lost our databases, they had to be taken offline, we could still find things if we needed to.

INTERVIEWER: Okay. What about actually shipping them? Did you use refrigerated trucks?

RESPONDENT: We used refrigerated trucks. Now as it turns out, that turned out most probably a little bit of overkill because most of the move occurred in February and March. So the weather was cool anyway. But we did move them in refrigerated trucks. And each, one of the approved DOT shipping containers is a steel drum. So we took each film in a can and put it inside, over packed it in a steel drum. And it's amazing how few film cans actually fit in a 55 gallon steel drum. It's like 14 or 15, 2000' cans. So needless to say, we moved a boatload of drums.

I mean, we kept recycling the drums. So we essentially bought enough drums for I think three semi loads. And a semi doesn't hold as many drums as you would think, you know, because they're pretty sizable. And, of course, they could only be on one layer. They couldn't be stacked readily. So we, I think, I want to say we bought like 120 drums or something and just, you know, recycled them. You know, we'd load, I want to say a semi held like 42.

And then, you know, moved 42, 42 drums were on the way from Dayton to Culpepper while 42 were being loaded in Dayton and 42 were being unloaded in Culpepper and just kind of, you know, rotated it around that way so. And it worked out really well. I want to say we got the entire thing moved in about 10 or 12 weeks. It was pretty impressive, actually. And didn't lose anything, and everything got put on, you know, got put on the shelf as expected. It was really a remarkable exercise in logistics.

INTERVIEWER: Nice. So how often are the nitrate films accessed? I mean, what are . . .

RESPONDENT: There are some things that probably have not been off their shelf since we moved it here. And then there have been other things that have either come up to our lab several times or have gone in and out of the vault for various reasons. Keeping in mind that even though we might have gift agreements and deposit agreements with the, and we do for virtually everything we have, we don't own the intellectual property rights for very much.

In fact, a very small percentage of the films do we actually control the rights to. So what that means is, for example, Universal's films that we store here are all under deposit agreement. And if they want to borrow something, they, you know, they have the right to do that. Likewise, Sony Pictures Entertainment, who owns the Columbia film collection that we, we own the Columbia film collection. But they own the intellectual property rights to it.

So even though we own the physical property, it was a gift, an outright gift from Columbia to the Library of Congress, Sony owns the intellectual property rights. So once again, they have rights to access the material. Now we work, you know, closely with the various people in the various preservation departments of the studios and try to mold them into and get them to understand archival sensibilities, and but when push comes to shove, if they want it, they typically can get it, and that's fine.

I don't begrudge them that at all. In fact, they do a lot of good work when it comes to preservation. So many times, we're able to actually get copies. Now not so much on film. Now it turns out to be either DVDs, Blu Rays, or in some cases files. But at least we get access materials in part, in exchange for basically being the caretakers

of their materials. An exception to that is Disney in the respect that they actually supply us with funding for staff.

INTERVIEWER: Oh, nice. Do you ever still loan prints for projection?

RESPONDENT: Yes, we do. We have a pretty active projection program. We do not loan nitrate prints for projection typically. Although, I believe we did send a title or two to the recent nitrate motion, nitrate show out at Eastman House.

INTERVIEWER: Okay. And is that because just of the age of the film or because people, very few theaters have the correct projectors . . .

RESPONDENT: Oh, virtually, you mean as far as for nitrate film in general or?

INTERVIEWER: Yeah.

RESPONDENT: Yeah, well, first off, for nitrate film, to be able to project nitrate film, you have to have a certified booth. And to my knowledge, the only ones that do in this country are UCLA, us and Eastman House. And David Packard, actually, his Stanford Theater actually has a nitrate certified booth. So they are very few and far between to begin with. But the other thing is, we're not going to loan a nitrate print for screening that we don't already, that we haven't already preserved.

And then on top of that, even if we have preserved it, and even if we have a print, there's a good chance it's actually not going to run through a projector anymore because it's just so old, and there are issues potentially with it. So we don't, you know, we have probably thousands of nitrate prints, and of that, maybe ten are actually in good enough condition to actually run through a projector safely with any kind of reasonable assurance so. Maybe 100, but I doubt it's that high.

INTERVIEWER: Yeah. So are there changes you'd like to see in regulations or the care of nitrate or education?

RESPONDENT: I think we're moving in the right direction. I don't know if you know Rachel Parker on our staff or talk with Rachel. But she's our liaison with NFPA, and she's been pretty, you know, boisterous in working with Heather Heckman and I think you guys out at Wisconsin, to try to get the, some semblance of reason to some of these NFPA-specified things that are no longer applicable because time has passed them by in some cases, and technology has improved.

And try to get things more, like the common ducts between vaults. I mean, that was a thing where back in the day, when they passed those regulations, made perfect sense because they didn't have fire dampers and alarm systems that could seal off a vault really effectively. So but now, we do. So let's take advantage of that. And so we've had some success, but there are still some things.

I mean, my biggest gripe with NFPA is that many of the people that are on the NFPA-40 Committee have never seen a roll of nitrate film, really have no knowledge of it. They're chemical industry folks. And while they may have a great body of knowledge

about chemistry works and fire issues, unless you, film is different in some ways, similar in many ways, different in some significant ways.

And the one thing that they're not concerned about is the fact that we are as concerned about the material itself as we are about fire safety and facility safety. Collection safety is a priority as well. And that's not what NFPA does. And I understand that. But if we can just at least impart some of that wisdom upon them and where it makes sense, continue to evolve the regulation to deal with that, that's great, and then we can move forward. Because what happens is, for example, NFPA says a long-term storage vault doesn't have to be cold essentially.

It doesn't really require certain temperature limits or limits that are good for archival storage really. Because they say that's not their role. And we understand that. However, what happens is, people look at that and say, well, I don't have to store my film in this condition because NFPA says it's okay. Well, that's not really the issue, okay. The NFPA says it's okay because it's not a, because A, it's not their responsibility or within their scope to deal with how to properly store a film collection. They're only concerned about making sure that if it catches fire, it doesn't kill people or burn a facility down or minimizing the risk for both of those.

They don't really care whether it's 100 degrees or 5 degrees as long as that doesn't impact, you know, fire safety. But as archivists, and as we are, so but what that means is that you cannot apply the NFPA temperature guidelines to an archival logic, because it doesn't meet it. It doesn't meet that rigor. So and that's where archivists really need to educate their people in their areas that are the facilities' people to understand that, yeah, NFPA says it can be 68 to 75. But that's not good enough for archival storage, okay. So don't build yourself an office building temperature-wise.

Build yourself an archival vault temperature-wise. And so that, and that's really what I see as an archivist's job is that education element, to make sure that people understand NFPA safety, archival storage concerns come under different codes. And look at everything. And then decide. And let's face it, everything comes down to money. And figure out what you can do to be the best caretaker you can for the collection as well as the buildings themselves.

INTERVIEWER: Okay. And last but not least, is there anything based on your own personal experience working with nitrate that you think people should know about nitrate?

RESPONDENT: Don't be afraid of it, basically. It is film at its heart. Respect it. don't panic if you see something that's deteriorating. You know, use your archival skills to determine whether or not you should leave that material in or whether or not it can be safely duplicated. And if so, duplicate it and then make a decision as to whether or not you take it out of the main roll just to keep the rest of the material around as long as possible.

Because nitrate deterioration is not a serious safety issue for people or buildings. It is an issue for the safety of the collection, the collection materials. So if something is starting to actively deteriorate to the point where you cannot only smell it, but see it, you need to really deal with it. And that can be freezing it at least temporarily, but it's got to

be a little bit more active process. Decide whether or not it warrants duplication. If it doesn't warrant duplication, then dispose of it safely.

INTERVIEWER: Okay. Do you have anything else to add?

RESPONDENT: I can't think of anything.

INTERVIEWER: Okay.

RESPONDENT: If you have any further questions, obviously, or follow-ups, just let me know. We can talk. E-mail or whatever. All right?

INTERVIEWER: Okay. Well, I think that's it then.